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Thermoplastic resins for thin film intumescent coatings – towards a better understanding of their effect on intumescence efficiency

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Abstract

This study investigates the role of the binder in the efficiency of intumescent coatings. It is generally known that an acid source, a carbon source and a blowing agent are the main ingredients of such paints. However, since the binder may react with these ingredients, it may significantly affect the intumescence process. To begin with, the effect of the nature of the monomers, which compose the binder, on the chemical reactivity between the binder and the intumescent additives is investigated using thermogravimetric analysis. It is found that the thermal stability is enhanced when the copolymer is prepared with substituted styrene. Subsequently, the effect of the binder is investigated from a physical aspect. Special attention is devoted to the expansion rate and the dynamic viscosity. Finally, the efficiency of protective behaviour of the intumescent coatings prepared with the copolymers is evaluated. It is found that the thermal insulation is greatly improved when using a mixture of linear and crosslinked copolymers as the binder in intumescent coatings particularly when these copolymers are prepared from monomers showing good reactivity with ammonium polyphosphate.

Keywords: Intumescence; Fire resistance; Coating; Binder; Rheological behaviour

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1. Introduction

An intumescent coating is one of the easiest, one of the oldest and one of the most efficient ways to protect materials against fire [1,2]. It presents several advantages: it does not modify the intrinsic properties of the materials, such as, for example, the mechanical properties; it is easily processed; and it may be used on a variety of materials such as metals, polymers [3], textiles [4] or wood [5].

The protection of metallic materials against fire has become an important issue in the construction industry. Indeed, prevention of the structural collapse of the building, which can occur if load bearing steel elements attain a temperature above 550 °C, is paramount to ensuring the safe evacuation of people from the building, and is a prime requirement of building regulations in many countries.

Intumescent coatings represent an increasingly used way to provide passive fire protection to the structural steel that is more and more used in modern architectural designs, whilst at the same time maintaining their aesthetic qualities.

Intumescence is defined as the swelling of certain substances when they are heated. Intumescent coatings

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form an expanded multicellular layer on heating, which acts as a thermal barrier [6,7] that effectively protects the substrate against rapid increase of temperature, thereby maintaining the structural integrity of the building.

Intumescent coatings consist of intumescent additives bound together by a binder [8]. Generally, three intumescent ingredients are used: an acid source (generally ammonium polyphosphate APP), a carbon source (such as dipentaerythritol) and a blowing agent (most often melamine). The formulation of these coatings has to be adapted in terms of their physical and chemical properties to form an efficient protective char. Several studies [9–11] have demonstrated that some polymers can contribute to the intumescent phenomena. The binder has also a number of functions to fulfil, particularly in controlling the char expansion and ensuring an uniform foam structure.

From this point of view, the binder would be a fundamental ingredient of the intumescent paint. The aim of this study is to provide a better understanding of the influence of the polymer binder on the mechanism of intumescence and on the efficiency of the fire protection provided by the resulting char.

Linear and crosslinked substituted styrene/acrylic copolymers are studied. The effect of the nature of the monomer on the chemical reactivity between the binder and the intumescent additives is first investigated using thermogravimetric analysis. Then, the effect of the binder is analysed from a physical aspect, special attention being paid to its rheological behaviour: i.e. expansion measurements and dynamic viscosity. Lastly, the efficiency of the thermal insulation of intumescent coatings prepared with these copolymers is evaluated and correlated with the chemical and physical properties of the protective charred layer.

2. Experimental

2.1. Materials

The properties of the binders (supplied by Eliokem) that have been used in this study are reported in Table. In binder resin B, methacrylate monomer substitutes part of the substituted styrene monomer of binder resin A. In binder resin C, styrene monomer substitutes substituted styrene monomer of binder resin A. The crosslinked resins have the same composition as the Newtonian resins but have a crosslinked structure.

Table 1
Characteristics of the polymer binders

Binder	Monomers	Rheology
A	Substituted STY/acrylate	Linear Newtonian
B	Substituted STY/acrylate/methacrylate	Linear Newtonian
C	STY/acrylate/methacrylate	Linear Newtonian
D	Substituted STY/acrylate	Crosslinked thixotropic
E	Substituted STY/acrylate/methacrylate	Crosslinked pseudoplastic
F	STY/acrylate/methacrylate	Crosslinked thixotropic

Ammonium polyphosphate (APP)/binder mixtures were processed using the following method: firstly, the binder was dissolved in xylene (used as received from Aldrich). Secondly, the APP (Hostaflam AP422 from Clariant) was dispersed into the solution. Thirdly, the solvent was evaporated at 60 °C until constant weight. The APP/binder mixture was then ground in liquid nitrogen using an ultra centrifugal mill (Retsch ZM100) to avoid degradation. APP was added to the binder at 5 wt.% phosphorus content.

Intumescent coatings were prepared using APP as acid source, melamine as blowing agent and dipentaerythritol as carbon source and applied to the surface of a metallic support ($10 \times 10\ \text{cm}^2$). Thick films of about 1 mm were obtained by deposition of $1100\ \text{g/m}^2$.

2.2. Thermogravimetric analysis

Thermogravimetric analyses were carried out at 10 °C/min under synthetic air (flow rate: $5 \times 10^{-7}\ \text{m}^3/\text{s}$, Air Liquide grade) using a Setaram MTB 10-8 microbalance. In each case the sample (around 10 mg) in the form of powder was placed in an open vitreous silica pan. The precision of the temperature measurements was 1.5 °C over the whole range of temperature.

In order to determine whether a potential increase or decrease in the thermal stability of the polymer is related to the presence of the additive, the weight difference curves between experimental and theoretical TGA curves were computed as follows:

$\Delta w(T)$: weight difference curve: $\Delta w(T) = W\text{exp}(T) - W\text{the}(T)$,
$W\text{exp}(T)$: TGA curve of polymeric binder/APP,
$W\text{the}(T)$: TGA curve computed by linear combination of the TGA curves of the binder and APP: $W\text{the}(T) = xW\text{poly}(T) + (1-x)W\text{add}(T)$, with x = polymer content,
$W\text{poly}(T)$: TGA curve of the polymeric binder,
$W\text{add}(T)$: TGA curve of APP.

2.3. Dynamic viscosity measurement

Rheological measurements were carried out using a Rheometric Scientific ARES-20A thermal scanning rheometer (TSR) in a parallel plate configuration (Fig. 1). A dynamic viscometer measures elastic and viscous behaviours by determining the response to both steady and oscillatory shear. The thermal scanning

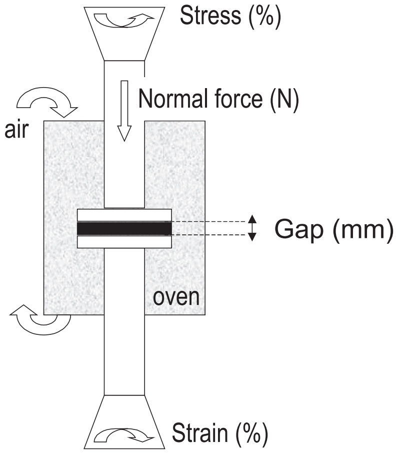

Fig. 1. Diagram of the rheometer in a parallel plate configuration.

rheometer measurements are designed (using the RHIOS V6-4.3 instrument configuration) to monitor the changes in rheological properties with temperature and/or time.

Samples of dry coating (diameter = 25 mm, thickness = 1 mm) were positioned between the two plates (25 mm diameter) with a starting gap of around 1 mm. A constant normal force was systematically applied in order to obtain good adhesion between samples and plates, and also to guarantee the validity of the results. First, the viscosity measurements were carried out by varying the value of the stress, of the normal force and of the frequency in order to define the best operating conditions for determining the viscosity values over the complete temperature range (20–500 °C). The best conditions are the followings: strain value: 10%, frequency: 10 rad/s. These conditions enable the material to be preserved during the formation of intumescence. The tests were performed in the 180–400 °C range with a heating rate of 10 °C/min.

2.4. Char expansion measurement

Char expansion measurements were carried out using the same apparatus (Rheometric Scientific ARES-20A). A low constant normal force (0.29 N) was applied to the sample in order to avoid the destruction of the char, and also to guarantee the validity of the results. The heating rate was also 10 °C/min in the range 20–500 °C. No strain was applied during these experiments.

2.5. Fire resistance

Temperature profiles were measured at the interface between the intumescent coating and the metallic plate for a sample exposed to a constant heat flux of 35 kW/m^2 under the conditions of the cone calorimeter (ISO 5660).

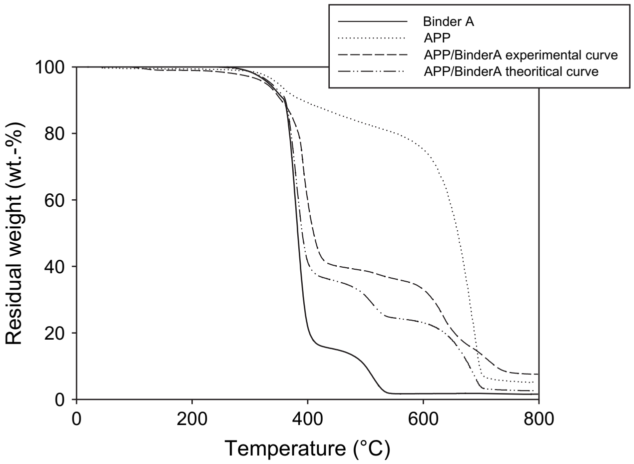

Fig. 2. TG curves of binder A, APP, binder A + APP (experimental and theoretical).

3. Results and discussion

3.1. Thermal degradation

In an intumescent process, the first stage consists of a reaction of the acidic species released by the acid source with the carbonisation agent with formation of a mixture of esters [12]. However, it has been reported that the polymer can contribute to the intumescence process [13]. The chemical reactivity of the resin with the APP is investigated here using thermogravimetric analysis. Figs. 2 and 3 give the thermogravimetric (TG) curves of some of the binder resins (A and C), of APP, and of the binder resin (A and C)/APP blends. The theoretical degradation curve of the mixture binder/APP is also presented. The difference between the experimental and the theoretical TG curves gives information on the reactivity of the binder resin with APP. When the experimental curve is higher than the theoretical one, the loss of weight is lower than expected showing that the

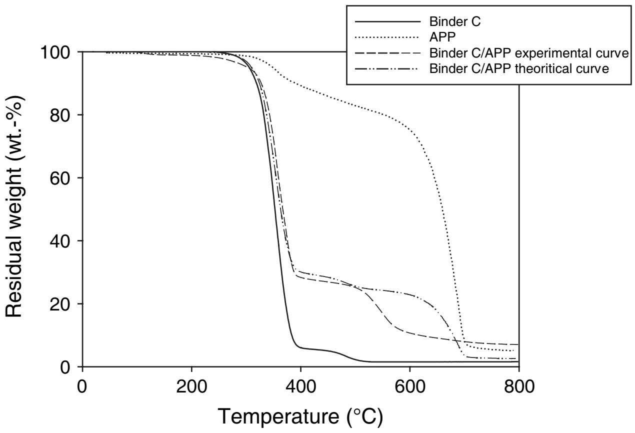

Fig. 3. TG curves of binder C, APP, binder C + APP (experimental and theoretical).

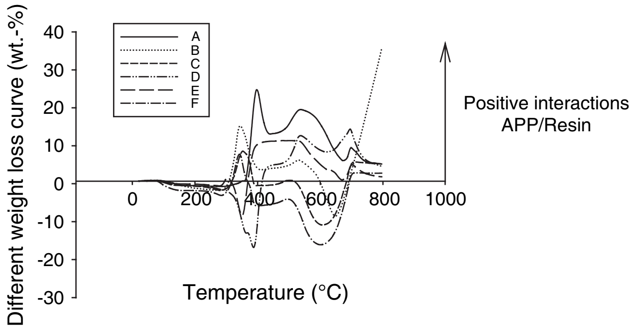

Fig. 4. Weight loss difference curves of resin/APP mixtures versus temperature.

reactivity of the resin with APP leads to thermal stabilisation of the materials. If the experimental curve is lower than the theoretical one, the reactivity of the resin with APP leads to thermal destabilisation of the materials. The difference of weight loss between the theoretical and the experimental TG curve is presented in Fig. 4. Differences are observed according to the type of resin. When the ratio of substituted styrene in the binder increases, the difference between the calculated and the experimental weight loss becomes larger (>20%) over a wider range of temperature. This is taken to be evidence of the synergistic stabilising effect between the substituted styrene and the APP.

Such an effect has previously been reported [13] and was explained by the fact that styrene monomers are trapped within a phospho-carbonaceous structure resulting from chemical reactions between substituted styrene and the degradation products of APP.

Similar results are obtained with the corresponding crosslinked resins D, E and F, except that an initial decrease in the thermal stability is observed between 300 and 410 °C for binder resin D and E. This behaviour is usually observed in intumescent systems [14,15] and is attributed to a catalytic effect of degradation of the acid evolved from the acid source, which initiates the intumescence phenomenon. In term of fire protection, such a catalytic effect is considered as a benefit since to be efficient the intumescent protective layer has to be formed in the early stages of a fire. For both resin/APP mixtures, a thermally stable protective layer is formed later on in the higher temperature range.

3.2. Dynamic measurements

The efficiency of the char is closely related to its ability to expand and form a multicellular structure and consequently to its physical properties during the intumescent process. One of the main aspect of intumescent char physical structure is its uniformity and its porosity. The char can be dense or porous. The type of char depends on the way the intumescence develops, which is closely linked to its chemical transformation during heating. The swelling of intumescent coating is due to the slowly diffusion of the evolved degradation gases released into the degraded matrix as presented in Fig. 5. The importance of the visco-elastic properties of this layer is then understandable [16–19] since it would affect the porosity of the obtained char. Moreover, previous studies have shown good correlation between the different steps of the intumescent process and measurements of the apparent viscosity [20–24].

The dynamic expansion of intumescent coatings prepared with the different binder resins is reported versus temperature in Fig. 6. The test is a measure of the ability of the coating to expand in spite of the load applied upon it during the intumescence. So the degree of expansion is related to the strength of the developing char. Relatively low expansion is observed with the linear resins, with a slightly greater expansion rate for the binder resin B. When adding crosslinked resin to the linear binder resin, the expansion is double, showing a higher strength of the developing char.

It is also important to note that whatever the binder resin, the intumescent protection development starts around 350 °C and a thermally and mechanically stable protective 'shield' is formed. To correlate the onset

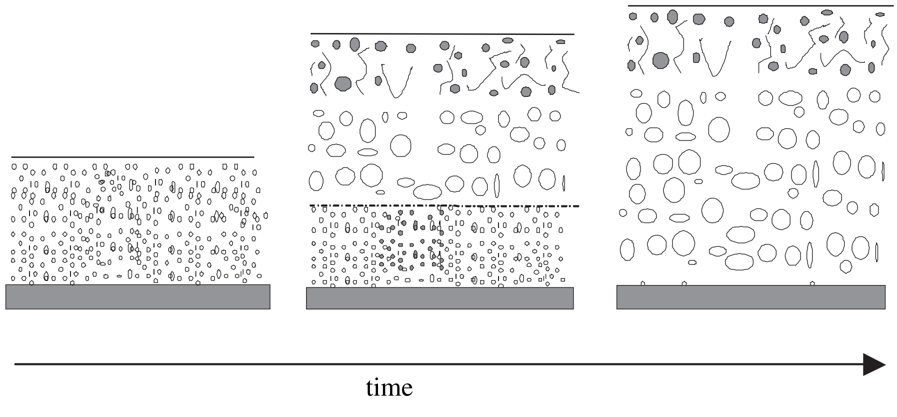

Fig. 5. Schematic representation of intumescent process.

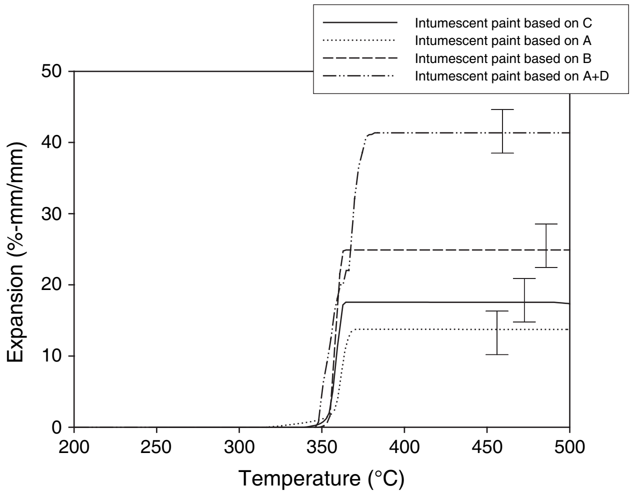

Fig. 6. Char expansion measurement of intumescent paints varying the binder resin.

expansion temperature with the onset degradation temperature of the component of the intumescent formulation, the TG curves of APP, melamine, binder resin and intumescent paint are compared with the expansion curves. The results for binder resin A are reported in Fig. 7. The expansion temperature is clearly linked with the onset temperature of degradation of the melamine and it explains why this temperature is similar whatever the binder resin of the intumescent coatings.

In order to understand why the expansion varies depending on the binder resin, the apparent viscosity of the binder resins, of the mixtures binder resin + APP and of the intumescent paints have been successively measured and are reported in Figs. 8–10.

The dynamic viscosity of binder resins alone is measured versus temperature (Fig. 8). Whatever the nature of the monomer, the viscosity is very low and no charring is observed in the temperature range corresponding to the development of the intumescence (between 350 and 400 °C). A slight increase in the apparent viscosity is observed when crosslinked resins are added to linear resins. The observed behaviours correspond to the one of thermoplastic materials. No obvious correlation can be found between these viscosity measurements and the difference in the char development observed with these resins. As a consequence, the viscosity of the mixture binder/APP was investigated (Fig. 9).

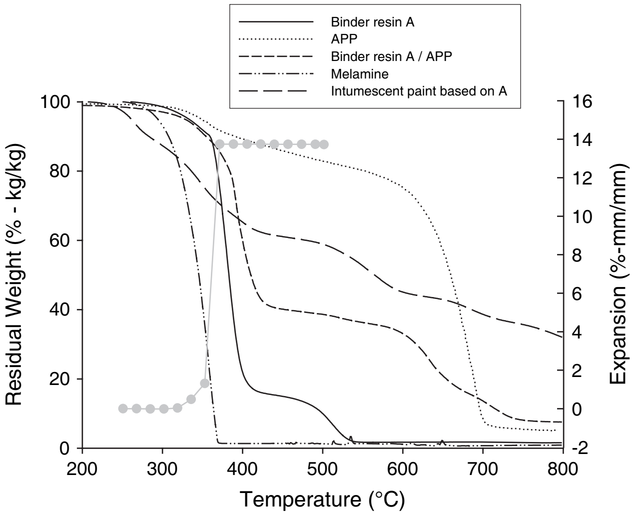

Fig. 7. Char expansion measurement and TGA curve of the intumescent paint based on binder resin A and TG curves of APP, binder resin A and melamine.

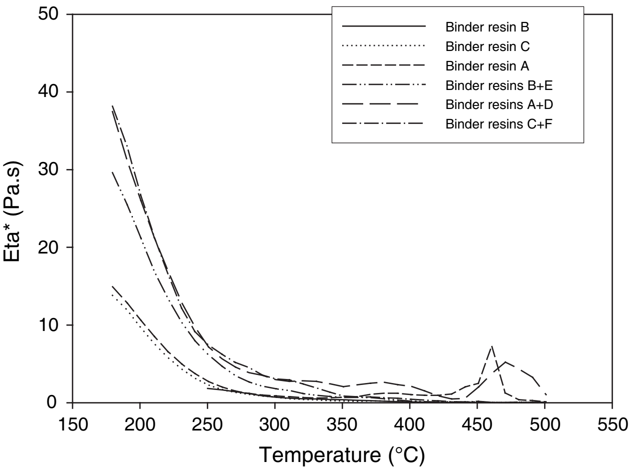

Fig. 8. Dynamic viscosity of the resins versus temperature.

A charring effect is observed for binder resin A between 300 and 350 °C. This can be correlated with the chemical reactivity of the substituted styrene based binder with the degradation products of the APP described earlier in Section 3.1.

The viscosity of the intumescent coatings versus temperature is shown in Fig. 10. For all the intumescent coatings, a two-step charring process is observed, in the temperature range 270–320 °C and 320–350 °C,

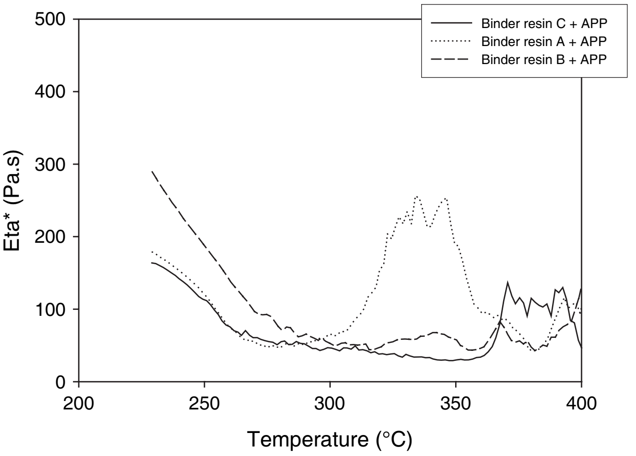

Fig. 9. Dynamic viscosity of the mixtures resin/APP versus temperature.

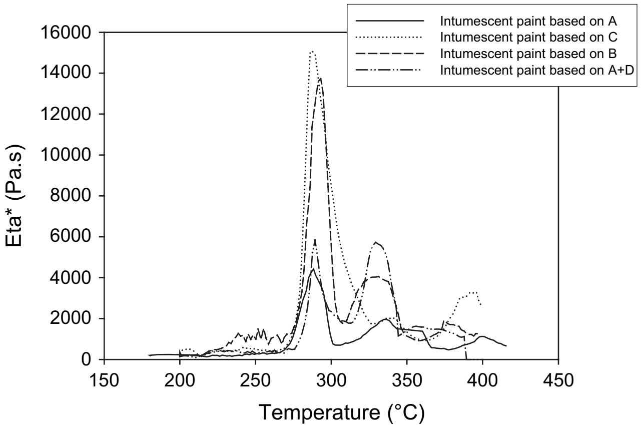

Fig. 10. Dynamic viscosity of the intumescent paints versus temperature.

respectively. The second viscosity peak deserves particular attention since it occurs in the range of temperature at which the char expansion starts. The best char expansion is obtained with the binder A + D, which shows the highest apparent viscosity in this range of temperature. It can be noted that the apparent viscosity of the intumescent paint based on binder resin B is much greater than that of binder A or C in the [320–350 °C] range of temperature. This can explain the better char expansion observed with this resin than with resin A or C.

This correlation between the coating viscosity (in the range of temperature at which the intumescence starts) and the efficiency of the char formation is perhaps not surprising. If the viscosity is too low, the gases escape from the char layer and feed the flame. If the viscosity is sufficient, slow diffusion occurs with the consequent formation of an expanded structure.

3.3. Fire protection

The temperature profiles measured at the interface of the intumescent coating and a metallic substrate are reported in Fig. 11.

The shape of the temperature profiles is similar for all the coatings. The temperature increases rapidly during the first 400 s and then the temperature stabilises and a plateau is achieved.

The temperature at the plateau is slightly lower with the coating prepared with binder C i.e. with the binder, which shows no reactivity with APP. So, looking at the temperature profiles obtained with the Newtonian resins, no correlation can be observed between the reactivity with APP, the expansion rate and the thermal insulation given by the coating. However, the difference of temperature at the plateau obtained with the different resins A, B and C is about 30 °C, which is within the experimental error.

When the coatings are formulated with a blend of Newtonian and crosslinked resins, a significant improvement of the thermal insulation is observed. This is particularly obvious with the binders A and B prepared with substituted styrene. The temperature at the plateau is decreased by about 100 °C.

The thermal insulation is enhanced when increasing the ratio of crosslinked resin in the binder mixture up to 40% as can be seen from Fig. 12. In practice, coatings cannot be prepared with higher amount of crosslinked resins because this leads to an unacceptable increase in the viscosity. However, paints formulated with too high amount of crosslinked resin are not likely to be very efficient as the film formation would be badly affected due to the crosslinked nature of these resins.

The crosslinked resins have the same monomer compositions as the Newtonian resins to which they are blended but have a crosslinked structure. The effect of the crosslinked resins is a modification of the rheology of the binder and thus of the coating during the intumescence process. This was shown in Section 3.2 above. The better thermal insulation obtained by the introduction of the crosslinked resin can be attributed to a better control of the diffusion of gases during the intumescence and consequently to an optimisation of the char development and structure.

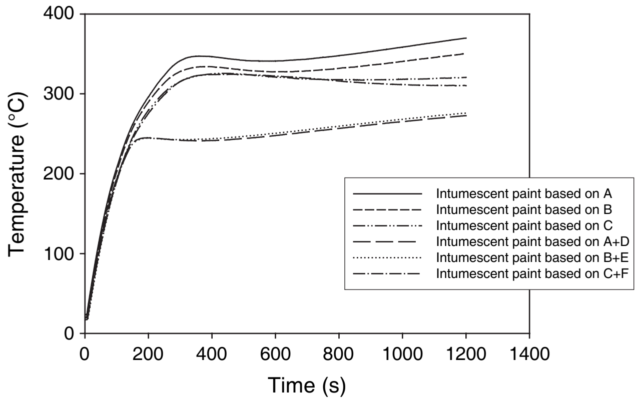

Fig. 11. Temperature profile measurements of intumescent paints varying the binder resin.

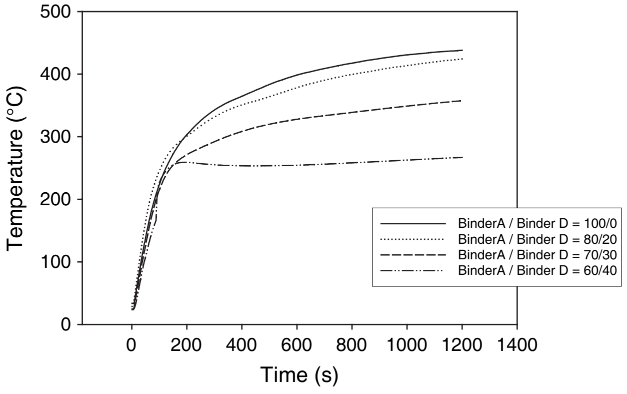

Fig. 12. Temperature profile measurements of intumescent paints varying the crosslinked resin content.

4. Conclusions

Results from this work substantiate the importance of both the chemical and physical properties of the coatings on the intumescent efficiency as already mentioned in a previous study [24]. The importance of the chemical nature of the polymer binder is highlighted by the reactivity with APP, which is better with substituted styrene than with styrene. The improvement of the thermal insulation, afforded by the char during a fire test, when a crosslinked resin is present in the binder, is clear evidence of the crucial role of the rheological properties of the binder under the testing conditions, particularly in the range of temperature at which the char formation starts. Optimum fire protection was obtained when the binder is composed of a mixture of Newtonian and rheological resins and contains substituted styrene as co-monomer.

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