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Intumescent fire protective coating: Toward a better understanding of their mechanism of action

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Abstract

The aim of this work is to better understand the role and the mechanism of action of boric acid and of coated ammonium polyphosphate (pure ammonium polyphosphate coated with THEIC) used as flame retardants in a commercial intumescent epoxy-based formulation using analytical techniques including thermogravimetric analyses (TGA) and solid-state NMR. In a previous paper, we detected that some reactions took place during the intumescence phenomenon between boric acid and ammonium polyphosphate upon heating. The paper focuses on the analysis of the degradation of those sole components and on the study of their interaction. It is first shown that the THEIC increases the thermal degradation rate of ammonium polyphosphate. This enables the degradation products of boric acid and coated ammonium polyphosphate to react together, resulting in the formation of borophosphate. It is suggested that the formation of this product provides the superior mechanical resistance of the char and promotes the adhesion of char on the steel plate.

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1. Introduction

Steel is a material commonly used in the construction of bridges, buildings, boats, cars, and it also plays an important role in other fields like marine or military furniture and offshore platforms. It is a non-combustible material which exhibits a good ductility but it begins to lose its structural properties between 470 and 500 °C [1]. That is because of this low failure temperature that 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 reach 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.

Several means exist for the protection of steel. They are called "passive fireproofing materials", which means insulating systems designed to decrease heat transfer from a fire to the structure being protected. These can be panels or blankets, but usually, coatings such as mineral-based or organic resin-based products, known as "intumescent coatings", are preferred. The use of fire retarded coatings is one of the easiest, one of the oldest and one of the most efficient ways to protect a substrate against fire [2,3]. 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 may also be used onto several materials including metallic materials [4], polymers [5], textiles [6] and wood [7]. Intumescent coatings are designed to perform under severe conditions and to maintain the steel integrity for one up to three hours when the temperature of the surroundings is in excess of 1100 °C [8–11]. When the temperature of the coating surface reaches a critical temperature under the heat of the flame, the surface begins to melt and is converted into highly viscous liquid. Simultaneously, reactions are initiated that result in the release of inert gases with low thermal conductivity. These gases are trapped inside the viscous fluid (formation of bubbles). The result is the expansion or foaming of the coating, sometimes up to several times its original thickness, to form a protective carbonaceous char (Fig. 1) that acts as an insulative barrier between the fire and the substrate [12].

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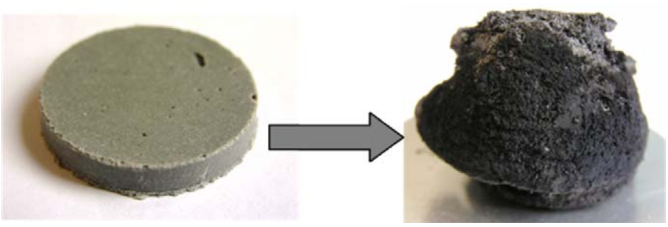

Fig. 1. Swelling of an intumescent coating.

The “intumescence concept” allows a balance between the fire properties and the level of additives in the material. Generally, three intumescent ingredients are used: an acid source, a carbon source and a blowing agent. The formulation of these coatings has to be adapted in terms of their physical and chemical properties to form an efficient protective char.

The mechanism of intumescence is usually described as follows [2,13–15]: first, the acid source breaks down to yield a mineral acid, then it takes part in the dehydration of the carbonization agent to yield the carbon char, and finally the blowing agent decomposes to yield gaseous products. The latter causes the char to swell and hence provides an insulating multi-cellular 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 a conservation of the underlying material.

In intumescent systems, it is essential that the different components incorporated show a suitable matching thermal behavior: a random selection of a component of each of the three classes mentioned above does not ensure intumescent behavior in their mixture. For example, it is obvious that the blowing agent must decompose at a temperature above that at which the charring of the mixture begins, but before the solidification of the liquid charring melt occurs.

In a previous paper [16], it was shown that the combination of ammonium polyphosphate derivative (APP) and boric acid provide an intumescent behavior to an epoxy-based coating. It was observed that their combination inside the resin leads to an important expansion, the formation of a hard char and enables a good adhesion of the char to steel plates, but this interaction has not been further explained. That is why it is essential to study the thermal stability of the different compounds. Thermogravimetric analysis (TGA) will be used in this paper to investigate the thermal stability of the different components as well as the formulation. The potential interactions between the compounds and the reactivity of the system will be also examined. It is expected to get information about the efficiency of the intumescent formulation. This experimental approach will be completed using solid-state NMR to characterize the chemical composition of the intumescent products formed at different characteristic temperatures. The first part of the paper details the analyses of each component and the second part investigates their potential interactions.

2. Experimental

2.1. Materials

Two fire retardant agents were used as received in this study:

- A mineral acid: boric acid (H_3BO_3, purity 95.5%) (Aldrich).
- A commercial ammonium polyphosphate (APP) derivative supplied by Clariant (Germany). It is a blended mixture of ammonium polyphosphate ($(NH_4)_{n+2}P_nO_{3n+1}$) and tris-(2-hydroxyethyl)isocyanurate (THEIC) (Fig. 2).

This compound will be referenced as “coated APP” in the paper.

The ingredients are used separately and then mixed together. Boron is put in excess compared to the phosphorous amount (proportions 1.5 (boron)/1 (phosphorus)).

2.2. Thermogravimetric analysis

Thermogravimetric analyses were carried out at 10 °C/min under 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). In order to determine whether a potential increase or decrease in the thermal stability happens between two additives mixed together, the weight difference curves between experimental and calculated TG curves were computed as follows [11]:

- $M_{\mathrm{add1}}(T)$: values of weight given by the TG curve of the first additive (e.g. boric acid).
- $M_{\mathrm{add2}}(T)$: values of weight given by the TG curve of the other additives (e.g. coated APP).
- $M_{\mathrm{exp}}(T)$: values of weight given by the TG curve of the mixture (add1 + add2 that is to say e.g. boric acid + coated APP).
- $\mathrm{M}_{\mathrm{th}}(T)$: theoretical TG curve computed by linear combination between the values of weight given by the TG curve of both additives: $M_{\mathrm{th}}(T) = xM_{\mathrm{add1}}(T) + (1 - x)M_{\mathrm{add2}}(T)$, where x is the “add1” (e.g. boric acid) content of the mixture.
- $\Delta(T)$: weight difference curve: $\Delta(T) = M_{\mathrm{exp}}(T) - M_{\mathrm{the}}(T)$.

The $\Delta(T)$ curves allow us to show a potential increase or decrease in the thermal stability of the system when two additives are mixed together.

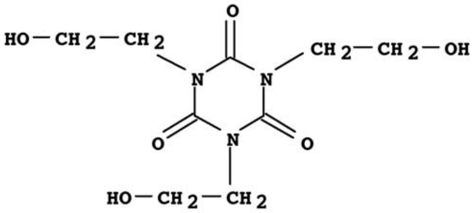

Fig. 2. Formula of THEIC.

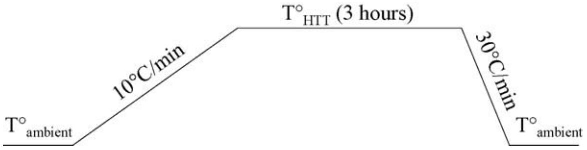

Fig. 3. Heat treatment program.

2.3. Solid-state NMR

In order to analyze the products of degradation of the intumescent systems at characteristic temperatures, heat treatments were carried out under synthetic air in a tubular furnace following the temperature-time program shown in Fig. 3.

The so prepared residues are analysed using solid-state NMR. High resolution ^{13}C, ^{31}P and ^{11}B NMR spectroscopies of the solids were performed.

^{31}P NMR measurements were performed using a Bruker Avance 100 spectrometer. Bruker probe heads equipped with 7 mm MAS (Magic Angle Spinning) assembly were used. ^{31}P NMR measurements were carried out at 40.5 MHz (2.35 T) using MAS (5 kHz) with ^{1}H dipolar decoupling. A repetition time of 120 s was used for all samples. H_3PO_4 in aqueous solution (85%) was used as reference.

^{13}C NMR measurements were performed on the same spectrometer as above mentionned with MAS at 10 kHz, high-power ^{1}H decoupling and ^{1}H–^{13}C cross polarisation (CP). All spectra were acquired with contact times of 1 ms. A repetition time of 5 s was used for all the samples. Typically, 1024 scans were necessary to obtain spectra with good signal to noise ratio. Tetramethylsilane was used as reference.

^{11}B NMR measurements were performed using a Bruker Avance 400 spectrometer at a spinning speed of 10 kHz. Bruker probe heads equipped with 4mm MAS (Magic Angle Spinning) assembly were used. ^{11}B NMR measurements were carried out at 128.3 MHz (9.4 T). A repetition time of 5 s and 128 scans were used for all samples. The reference used was H_3BO_3.

3. Results and discussion

3.1. Study of the degradation of boric acid and coated ammonium polyphosphate

Borax, boric acid and borates derivatives are well established as flame retardants [17] and nowadays zinc borates [18,19] emerge for the replacement of antimony oxides as synergists for halogenated fire retardant additives. When incorporated in polymers they can give off water upon heating, which provides a heat sink, a fuel diluent, a propellant for the fuel out of the flame zone, and a blowing agent for the glassy intumescent coating.

Various phosphorus-based flame retardants have been shown to exert physical and chemical actions both in the flame and in the condensed phase: flame inhibition, heat loss due to melt flow, surface obstruction by phosphorus-containing acids, acid-catalyzed char accumulation, char enhancement and protection of char from oxidation have all been seen in different polymer systems containing phosphorus-based flame retardants, although the relative contribution of each mode of action depends on the polymer system and the fire exposure conditions [20,21]. The coated ammonium polyphosphate used in this study is a high molecular weight chain phosphate, containing an important amount of nitrogen and phosphorous [22]. It is a source of phosphoric acid catalyst that speeds up the formation of carbonaceous char. THEIC is a carbonisation agent in the intumescent system and may be a synergist (P/N) as previously reported in the literature [23]. It reacts with APP leading to the formation of an intumescent structure.

Thermal stability of the intumescent char depends on the chemical structure of the char (e.g. the presence of cyclic structures is known to increase the char stability). In the following, degradation of coated APP, of boric acid and of the combined system coated APP/boric acid will be studied in order to get information on the thermal stability of various chars and to investigate the reactivity between the two components.

3.1.1. Thermogravimetric analyses

3.1.1.1. Boric acid. TG curve of boric acid is presented in Fig. 4. A two-step degradation mechanism is observed: a first step between 100 and 140 °C corresponding to a weight loss of about 30 wt.% and a second step in the temperature range (140–200 °C) leading to a thermally stable material (55 wt.% of the initial mass). Since there is a significant residue (55%), it is possible to assume that boric acid and/or its degradation/reaction products are main components of the final protective structure developed when the intumescent coating is exposed to a fire.

The first step of degradation is attributed to the dehydration of boric acid into metaboric acid (1). It is consistent with the mass loss (about 30%) measured by TGA. The second step corresponds to the dehydration of HBO_2 into boron oxide B_2O_3 (2):

$$H_3BO_3 \rightarrow H_2O + HBO_2 \quad (1)$$

$$2HBO_2 \rightarrow H_2O + B_2O_3 \quad (2)$$

B_2O_3 is a very hard glass, the crystals begin to break down at 300 °C, and a series of suboxides are produced with partial

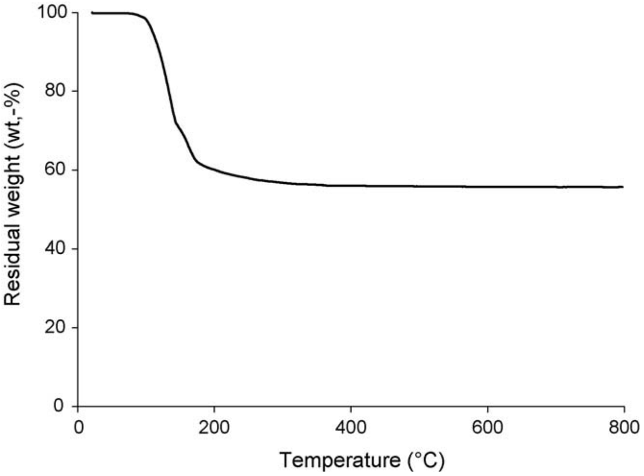

Fig. 4. TGA of boric acid.

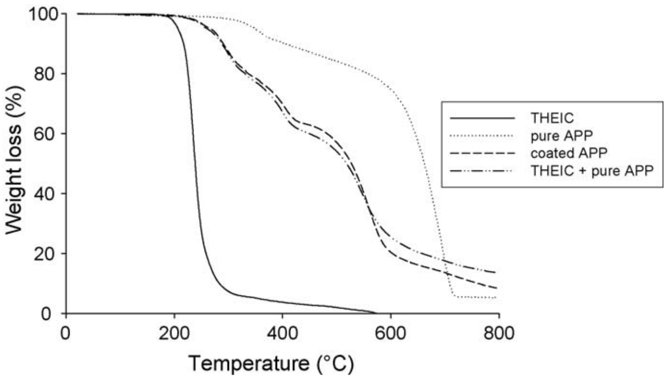

Fig. 5. Comparison between pure APP, coated APP and pure APP + THEIC.

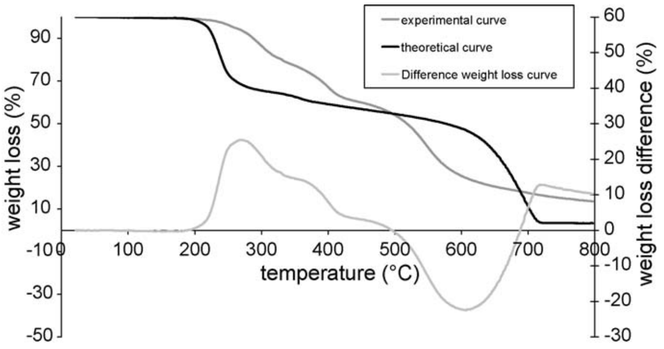

Fig. 7. TG and difference weight loss curves of the mixture pure APP and THEIC.

melting until full fusion is reached at 700 °C. Such a thermally stable compound is interesting to use in an intumescent system, because obtaining a high residue means that the amount of remaining char will be high. Moreover, due to the boron oxide, the char will also show in that case a good mechanical resistance.

Boric acid turns by dehydration into boron oxide between 140 and 200 °C, leading to a hard and high thermally stable residue. The amount of residue is high, which can be an important parameter in the formulation of an intumescent coating. As boric acid releases water and forms a hard glass, it can play the role of blowing agent, provide a "glue" to hold the combustion char together and provide structural integrity to the char.

3.1.1.2. Coated APP. Comparison between TG curves of uncoated APP, coated APP and of the mixture APP (64%)/THEIC (36%) is presented in Fig. 5.

The mechanism of degradation of pure APP has been widely investigated [1,24]. APP begins to lose ammonia at a temperature slightly above 200 °C, resulting in a highly condensed polyphosphoric acid. This material does not present additional weight loss below about 600 °C. Above this temperature, an azeotropic P_4O_{10}–H_2O mixture boils and phosphorous is lost from the system. The loss due to evolving NH_3 ranges from 2.8 to 14.3% of the total weight of the mixture.

The loss of NH_3 upon heating of APP is summarized in Fig. 6.

The degradation of the coated APP occurs in three steps: a first step between 200 and 300 °C corresponding to about 20% of weight loss, a second step occurring between 300 and 400 °C corresponding to a weight loss of about 20% and finally a third step occurring between 400 and 600 °C leading to a final residue of about 10% at 800 °C. The degradation rate between 600 and 800 °C is very slow.

In the case of coated APP, three degradation steps are observed compared to two for uncoated APP. It is interesting to observe that the degradation of coated APP occurs at lower temperature than that of pure APP. It seems that a reaction between uncoated APP and THEIC occurs.

The calculation of the difference weight loss curve of uncoated APP, THEIC and the mixture of the two components (Fig. 7) shows unambiguously that a reaction occurs.

There is a stabilisation between 200 and 500 °C and another one around 700 °C. The addition of THEIC allows a more regular degradation rate than in the case of uncoated APP.

It is also interesting to observe that the second step of degradation of APP corresponding to the sublimation of P_2O_5 in the temperature range (550–650 °C) takes place earlier in the presence of THEIC. A major step of degradation is observed in lower temperature range (500–600 °C) which might be attributed to the degradation of phospho-carbonaceous species produced when APP is degraded in presence of a carbon source (Fig. 8).

These products are formed by reaction between the degradation products of APP and THEIC. As a consequence, the nitrogenated agent has a strong catalytic effect on the degradation of APP. A little higher amount of residue is formed for coated APP in comparison with uncoated APP.

Looking at the conclusions obtained from the TG curves, it is noteworthy that coated APP is an acid source (there is creation of phosphoric acid), a blowing agent (due to the release of ammonia) and also a carbonisation agent (the THEIC contains atoms of carbon, which provide a char when heated). As mentioned in the introduction, an intumescent system needs a carbon source, an acid source and a blowing agent to develop. Coated APP plays by itself these three roles. As a consequence, it constitutes intrinsically an intumescent system.

3.1.2. Solid-state NMR

3.1.2.1. Boric acid. Borates contain trigonal BO_3 and/or tetrahedral BO_4 units [25], which can form a wide number of different structures ranging from isolated orthoanions to chains, rings,

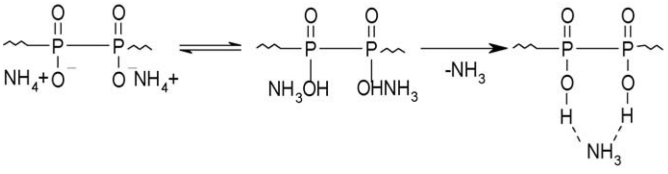

Fig. 6. Mechanism of degradation of APP.

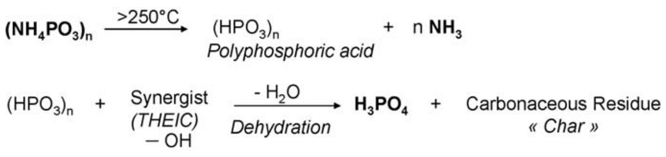

Fig. 8. Formation of phosphocarbonaceous species.

layers, and frameworks of these units. These structural types of BO_3 and BO_4 groups are found in crystalline alkalimetal borates, borate minerals as well as borate glasses.

BO_3 and BO_4 units can be distinguished by their ^{11}B quadrupole coupling parameters, which reflect the interaction between the nuclear electric quadrupole moment (Q) and the electric field gradient (EFG) tensor (V) at the nuclear site. The quadrupole coupling tensor is a traceless second-rank tensor that can be expressed by the quadrupole coupling constant, $C_Q = eQV_{zz}/h$, and the asymmetry parameter, $\eta_Q = (V_{yy} - V_{xx})/V_{zz}$, which describe the magnitude and symmetry of the interaction, respectively, and thereby the distortion of the local BO_3 and BO_4 units. Generally, BO_4 tetrahedra in borates exhibit C_Q (^{11}B) values less than 1 MHz whereas BO_3 groups possess quadrupole couplings in the range $2.4 \leq C_Q \leq 3.0$ MHz. Furthermore, the two types of boron environments can be distinguished by the ^{11}B isotropic chemical shifts (δ_{iso}) because BO_3 units resonate in the range $12 \leq \delta_{iso} \leq 25$ ppm, whereas BO_4 groups exhibit shifts in the approximate range $-4 \leq \delta_{iso} \leq 6$ ppm. This implies that separate resonances for BO_3 and BO_4 species generally can be achieved by high speed ^{11}B MAS NMR at high/intermediate magnetic fields ($B \geq 9.4$ T), which facilitates the quantification of these species in borate materials. The spectra have been simulated using the simulation software QUASAR [26] to determine the evolution of BO_3 and BO_4 species versus temperature.

^{11}B solid-state NMR has been carried out on the residue of boric acid obtained at various heat treatment temperatures (HTTs). Considering the steps of degradation of boric acid observed on the TG curves (Fig. 4), four heat treatment temperatures (95, 120, 200 and 450 °C) have been chosen for the solid-state NMR analysis. The spectra of the treated samples have been compared to the reference spectra of boron oxide and boric acid at ambient temperature. The weight loss (WL) corresponding to the heat treatment is indicated on the Fig. 9.

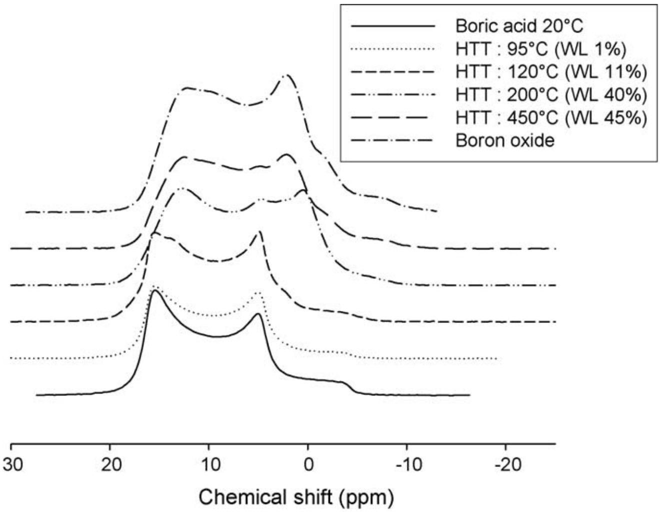

Fig. 9. ^{11}B solid-state NMR of boric acid at different HTTs.

The spectrum of boric acid at ambient temperature shows a second-order quadrupolar lineshape that is typical of boron atoms in a trigonal bonding configuration. After heat treatment at 95 °C, the weight loss is not significant: this temperature corresponds to the beginning of the dehydration of boric acid into metaboric acid. The spectra for a HTT = 95 °C and at ambient temperature are similar, which is in good agreement with the proposed mechanism of degradation since boron has the same structure in H_3BO_3 and in HBO_2. At 120 °C, metaboric acid is created by dehydration of the boric acid, other species presenting an isotropic displacement appear at 13 and 2 ppm [27], and this phenomenon becomes quite important at 150 and 200 °C. These bands correspond to the formation of B_2O_3 species: in this range of temperatures, several boron structures exist [28,29]. At HTT = 300 and 450 °C, a sharp modification of the spectrum is observed. Comparison of this spectrum with the one of B_2O_3 demonstrates that the thermally stable residue is boron oxide.

The spectra of boric acid at 20 °C and boric acid heated at 95, 120, 200, 300 and 450 °C were simulated using the protocol described above. Examples of the results of the simulation for boric acid treated at 20 and 200 °C are presented in Figs. 10 and 11.

At high temperatures ($T > 200$ °C), two different BO_3 species and two different BO_4 species are detected: BO_3(ii) in B_2O_3 and BO_3(i) specie in which boron atoms do not have the same environment as in boron oxide (for example H_3BO_3), and BO_4(ii) in B_2O_3 and BO_4(i) specie which is in a different conformation.

The Table 1 summarizes the modelling parameters and results obtained at different heat treatment temperatures: HTT = 20, 200 and 450 °C.

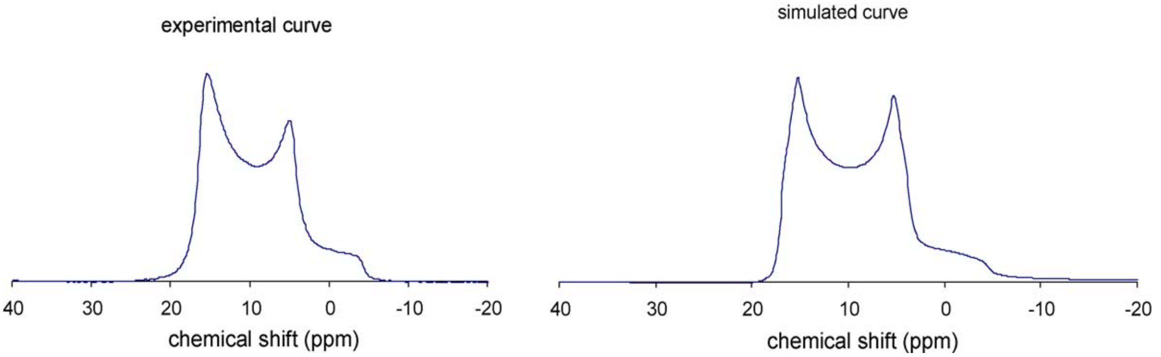

Fig. 10. Simulation of the ^{11}B spectrum of Boric acid at 20 °C.

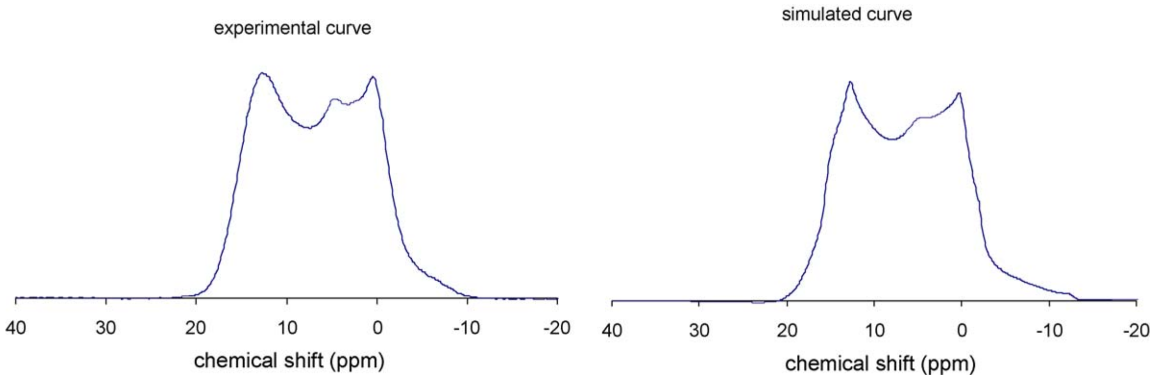

Fig. 11. Simulation of the ^{11}B spectrum of boric acid at 200 °C.

The percentage of BO_3(i) species decreases whereas the percentage of BO_3(ii) species increases during heating. This result makes sense, since when temperature increases, boric acid turns into B_2O_3: the BO_3 species detected at low temperature (i) are BO_3 in the boric acid conformation, which turn during heating into BO_3 in the B_2O_3 conformation (ii).

The same table presents the evolution of two BO_4 species (i) and (ii). The BO_4 species detected at low temperature (i) are BO_4 in the boric acid conformation, which turn during heating into BO_4 in the B_2O_3 conformation (ii).

3.1.2.2. Coated APP. ^{13}C NMR (Fig. 12) and ^{31}P solid-state NMR (Fig. 13) were carried out on coated ammonium polyphosphate treated at different temperatures. The spectra obtained for the different heat treatment temperature have the same profile. The spectrum at HTT = 300 °C is presented in Fig. 12 as typical example.

Table 1
Modelling parameters and results at three different temperatures

Temperature	BO_3(i)	BO_3(ii)	BO_4(i)	BO_4(ii)
20 °C				
%	96.2	0	3.8	0
δ_{iso} (ppm)[a]	19.7	0	3.131	0
C_Q (MHz)[b]	2.54	0	0.804	0
η_Q[c]	0	0	0.9	0
GB(Hz)[d]	60	0	430	0
200 °C				
%	63.7	24.5	9.8	2
δ_{iso} (ppm)	18.8	19.1	2.96	3.05
C_Q (MHz)	2.61	2.56	0.8	0.79
η_Q	0.12	0.1	0.87	0.88
GB (Hz)	83	69	453	402
450 °C				
%	70.3	21.1	5.6	2.9
δ_{iso} (ppm)	18	18.4	2.72	3.1
C_Q (MHz)	2.7	2.6	0.79	0.78
η_Q	0.17	0.15	0.83	0.85
GB (Hz)	96	75	599	550

[a] Isotropic chemical shift.
[b] Quadrupolar coupling constant.
[c] Quadrupolar asymmetry parameter.
[d] Gaussian broadening.

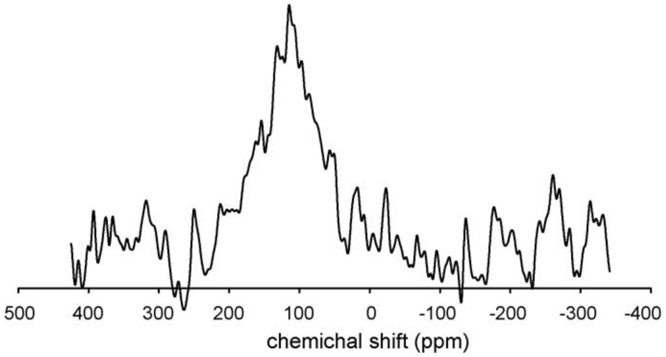

Fig. 12. ^{13}C NMR of a residual char HTT = 300 °C.

The CP–DD–MAS ^{13}C NMR spectrum exhibits a broad band centred at 110 ppm. It implies the presence of several non-magnetically equivalent carbons. This band can be assigned to several types of aromatic and polyaromatic species which can be partially oxidized. It suggests the condensation of aromatic species to polyaromatic species. This broadening may also be explained by the fact that a disorganized structure is created. It

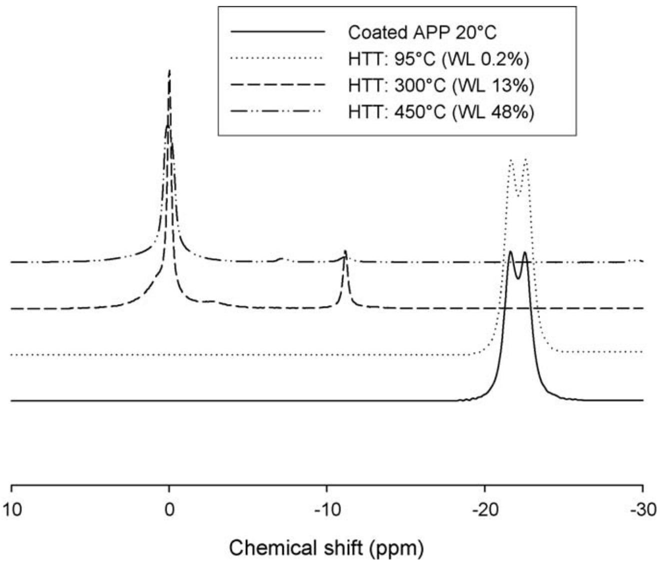

Fig. 13. ^{31}P solid-state NMR of coated APP treated at different temperatures.

is impossible to distinguish any differences on the spectra, as the carbonaceous components seem to remain in the same broad bands at the different HTTs.

DD–MAS ^{31}P solid-state NMR of coated APP has been carried out on the residue obtained at different heat treatment temperatures (Fig. 13) in order to analyze the evolution of phosphorus species.

At ambient temperature, the spectrum of coated APP is characterized by a split signal, corresponding to polyphosphate chains [30]. For a HTT of 95 °C, the spectrum is not modified, which is in good agreement with TGA since very low degradation was detected at this temperature (WL = 0.2%). At 300 °C, the peaks corresponding to APP disappear and additional peaks appear at 0 and −12 ppm. These peaks, respectively, correspond to the peaks of phosphoric acid (H_3PO_4) and/or to P–O–C bonds in orthophosphates bound to alkyl groups and to pyrophosphate and/or P–O–C bonds in orthophosphate including aromatic substituents [31,32]. It confirms that the first step of degradation of APP corresponds to the breaking of the phosphate chain which leads to the formation of phosphoric acid and/or pyrophosphoric acid. Moreover, it confirms that the THEIC reacts with APP to form a phosphocarbonaceous structure. At HTT = 450 °C, only phosphoric acid is observed.

3.2. Study of the degradation of the mixture boric acid/coated APP

As it has been shown in the previous section, coated APP and boric acid used as individual component can both play a significant role in the mechanism of intumescence. This section is therefore devoted to the study of the potential interactions between these two components using TGA and solid-state NMR.

3.2.1. Thermal degradation of the mixture

The TG curve of the boric acid mixed with coated APP is presented in Fig. 14.

The degradation of the mixture occurs in four main steps: two steps overlap between 100 and 180 °C corresponding to a weight loss of 30 wt.%. Two weak steps occur between 200 and 450 °C and between 450 and 800 °C, corresponding to a weight loss of about 15%. This degradation leads to a residue of about 55%.

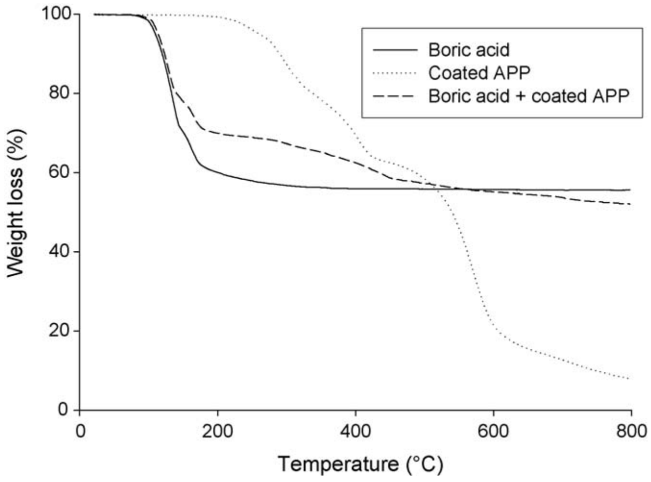

Fig. 14. TG curves of boric acid, coated APP and the mixture boric acid + coated APP.

The comparison of the experimental TG curve with the theoretical TG curve (Fig. 15) shows a low decrease in the thermal stability between 100 and 120 °C while a sharp increase in the thermal stability is observed from 550 to 800 °C.

The residue is about 10% higher than what could be expected from the theoretical curve. As a consequence, it can be assumed that chemical interactions between the two components occur and lead to the formation of high thermally stable materials from 550 to 800 °C.

3.2.2. ^{11}B solid-state NMR

Fig. 16 exhibits ^{11}B solid-state NMR spectra of the mixture boric acid/coated APP heat treated at different characteristic temperatures (only spectra at HTT = 95 and 450 °C are presented because they exhibit the most significant evolution). Those spectra are compared with that of pure boric acid.

The spectra show unambiguously that a reaction takes place between boric acid and coated APP, or between the degradation products of these compounds. NMR spectrum of the mixture heated at 95 °C is similar to the spectrum of boric acid heated at 95 °C prepared under the same conditions. There is no reaction between boric acid and coated APP at this temperature. Some additional tests have been carried out at 450 °C: it is noteworthy that the spectrum of the mixture of boric acid and coated APP heated 3 h at 450 °C exhibits a peak at $\delta_{iso} = -3$ ppm assigned to borophosphate (Fig. 17).

It demonstrates that the ammonium polyphosphate and/or its degradation product contained in the coated APP effectively react with boric acid and/or boron oxide to yield borophosphate [32]. At 450 °C, there is also boron oxide remaining, indicated by peaks of low intensity characteristic of boron oxide.

The simulations of boron species at 450 °C are not presented here, as the main point of interest of this paragraph was to show the presence of borophosphate, which is clearly identifiable on the spectrum.

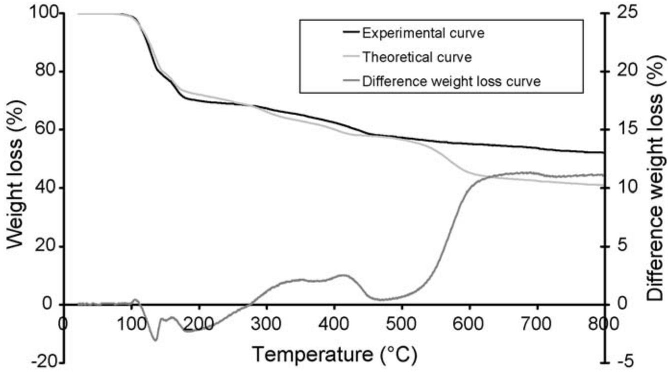

Fig. 15. TG and difference weight loss curves of boric acid, coated APP, and boric acid + coated APP.

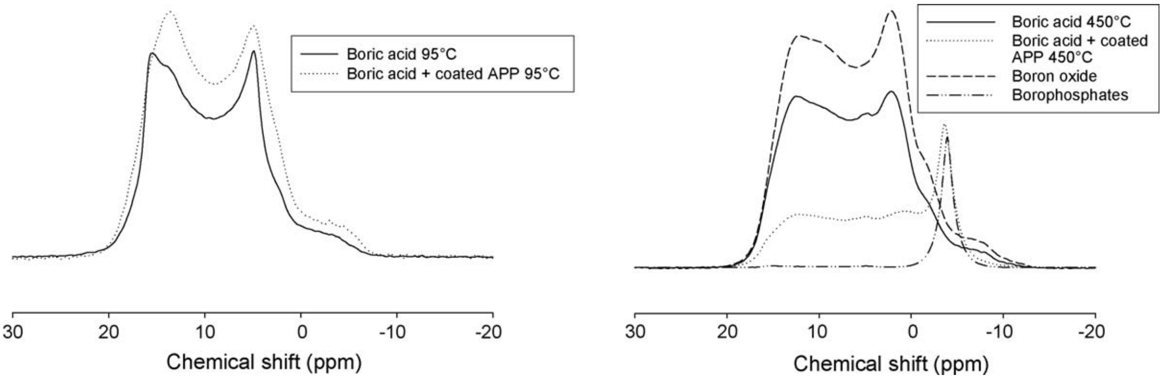

Fig. 16. ^{11}B solid-state NMR spectra of boric acid mixed with coated APP at 95 and 450 °C.

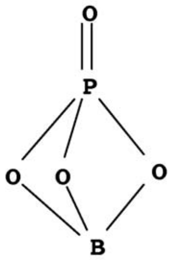

Fig. 17. Structure of borophosphate (BPO_4).

3.2.3. ^{31}P solid-state NMR

The same mixtures as mentioned above have been examined using ^{31}P solid-state NMR (Fig. 18).

The spectrum of borophosphate exhibits a single band at −30 ppm assigned to B–O–P bonds [33,34]. When heated at 450 °C, the spectrum of the mixture of boric acid/coated APP exhibits a band at the same chemical shift demonstrating unambiguously that a reaction takes place between boric acid and ammonium polyphosphate: all the phosphorous has reacted with boron to yield borophosphate. This also explains the fact that, as boron is in excess compared to phosphorus, there are some boron oxides remaining at 450 °C in the ^{11}B solid-state NMR spectra (Fig. 16).

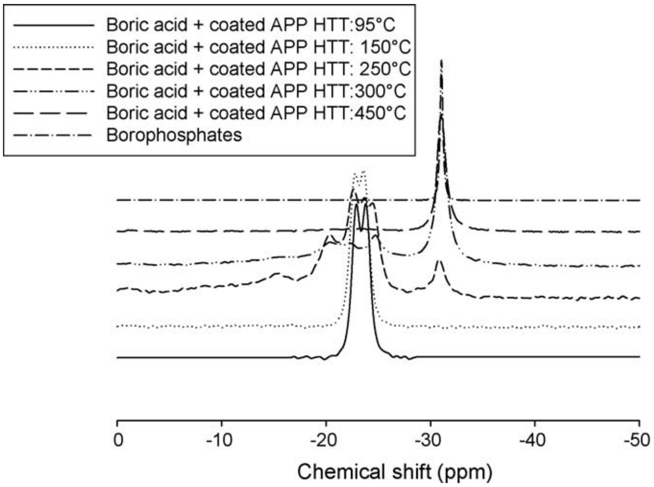

Fig. 18. ^{31}P NMR of a mixture of boric acid and coated APP treated at five different temperatures.

However, considering only the results obtained at 95 and 450 °C does not enables to determine if borophosphate is formed through a reaction between boric acid and coated APP or between the degradation products of these compounds: in order to determine at which temperature borophosphate is formed, the mixture of boric acid and coated APP was treated at three other temperatures: 150, 250 and 300 °C (Fig. 18).

The peak corresponding to borophosphate appears in the spectrum at 250 °C, i.e. when all the boric acid has turned into boron oxide and the coated APP is turning into phosphoric acid. A broad band between −18 and −27 ppm is observed for the heat treatment at 300 °C, which can be assigned to polyphosphoric acid having different level of cross-linking.

At 450 °C, only crystalline borophosphate and boron oxide glass remain. Considering the TG curves of boric acid and coated APP, it means that the reaction yielding borophosphate is a reaction between the degradation products of boric acid and coated APP. Boron oxide and phosphoric acid react together to yield borophosphate (Fig. 19).

As boron has been taken in excess compared to phosphorus, some B_2O_3 remain at 450 °C. Fig. 19 explains why it is important to add some THEIC in the APP: considering the TG curve of APP and coated APP (Fig. 5), it is clear that coated APP degrades earlier (about 200 °C) than pure APP (about 300 °C). This allows a rapid production of phosphoric acid, and so a possible reaction at low temperature (250 °C) between this component and boron oxide. In this case, the earlier the reaction, the better it is for obtaining an efficient intumescent system.

To see the influence on the spectra of varying the proportions of coated APP and boric acid, experiments have been carried out at 250 °C (temperature at which borophosphate begin to appear) with different amounts of each compound—boron/phosphorus

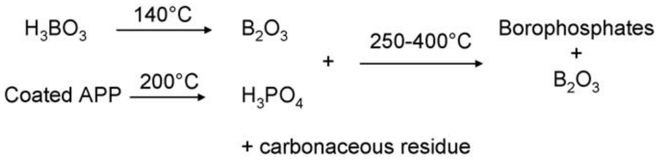

Fig. 19. Scheme of reaction of creation of borophosphates.

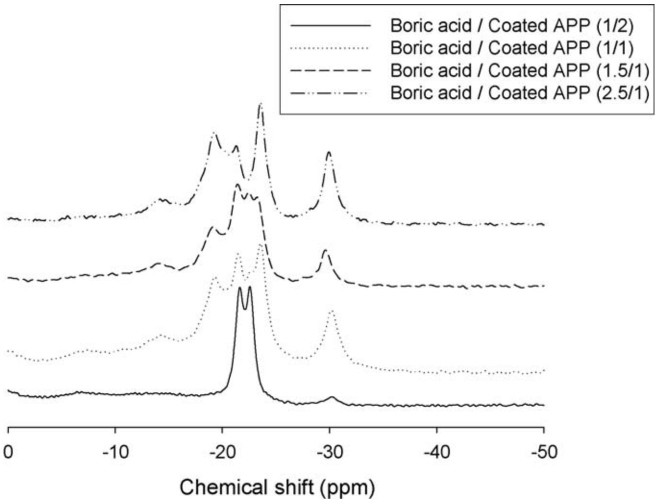

Fig. 20. ^{31}P MAS–NMR spectrum of boric acid and coated APP mixed in different proportions heated at 250 °C.

(w/w): 1/2, 1/1, 1.5/1 (proportions used in the commercial formulation) and 2.5/1.

The collected residues have been then analyzed by ^{31}P NMR (Fig. 20).

The peaks characteristic of the coated APP remain when the proportions 1/2 are used. Only a small peak characteristic of borophosphate is observed at −30 ppm: this might be explained by the fact that phosphorous is in excess compared to boric acid, the main part of the borophosphate might be created at a slightly higher temperature.

This is confirmed by another experiment: the ^{31}P NMR spectrum of boric acid and coated APP mixed in the ratio 1/2 and heated at 300 °C (Fig. 21) shows a high peak characteristic of borophosphates at −30 ppm and the peak characteristic of phosphoric acid at 0 ppm: as coated APP is in excess, the part which does not react with boric acid turns into phosphoric acid.

Concerning the proportions 1/1 and 1.5/1, borophosphate (peak at −30 ppm) appears and the peaks characteristic of the coated APP begin to disappear.

In case of the 2.5/1 proportions, the boron is in excess, no more peaks characteristics of the coated APP can be observed, but there is an intense peak at −30 ppm corresponding to borophosphate and additional peaks appearing at −25 and −18 ppm: all the phosphorous has reacted and different forms of networks are created.

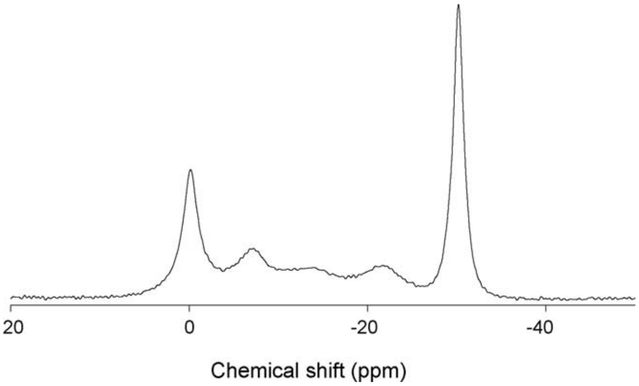

Fig. 21. ^{31}P MAS–NMR spectrum of boric acid and coated APP mixed in the proportion 1/2 heated at 300 °C.

In solid-state NMR, the atoms interact together and the level of interaction depends on the number of “neighbours” of the concerned atom. These interactions are said to be Q^1 interactions, if there is only one neighbour, Q^2 if two neighbours, etc. [35]. In phosphate material, the network is made of PO_4 tetrahedra that can be classified according to the number of bridging oxygen atoms per PO_4 unit (Q^n). Chemical shift at −15 and −26 ppm is evidence of the formation of Q^2 middle groups containing two bridging and two non-bridging oxygen atoms. The broad band centred at −30 ppm appears suggesting the presence of Q^3 branching groups whereas peaks around 0 ppm are characteristic of atoms in Q^1 form.

3.3. Discussion

In a precedent paper [16], four intumescent formulations were studied: a thermoset resin alone, the thermoset resin mixed with boric acid, the thermoset resin mixed with a coated APP and the resin mixed with both boric acid and coated APP. Different experiments, such as TGA, rheological analyses, mechanical resistance of the char and fire resistance in industrial furnaces have been carried out on these four coatings. Conclusions made after these tests were the following:

- During fire tests in industrial furnaces, ammonium polyphosphate and boric acid provide good performance when they are incorporated separately into the resin, but the intumesced char falls off the plate. Using a torch test onto the plate, it was revealed that the intumesced char formed from the thermoset resin containing coated APP is light and blows away during the experiment. It was also shown that the adhesion of the coating to the steel plate is very weak when phosphorous species are not added inside the formulation. The char developed from resin mixed with boric acid slides along and does not remain stuck on the plate. The best result was obtained when APP and boric acid were combined into the resin: the fire performances were much better than the performances of the three other formulations and the char remained well stuck on the plate.
- It was shown that the char of resin mixed with boric acid had an excellent mechanical resistance, whereas the char of the resin mixed with coated APP was light, with poor mechanical resistance. The best result was obtained when both additives were combined into the resin, leading to a high expansion, with a char showing a good mechanical resistance. Moreover, the combination of boric acid and coated APP during heating has been shown to promote adhesion between the coating and the steel plate.

Using analytical methods (TGA and solid-state NMR), we have shown in this work that boric acid and coated APP interact upon heating. It has been shown that boric acid turns into boron oxide around 140 °C, leading to a hard and high thermally stable residue. Coated APP turns into phosphoric acid and phosphocarbonaceous compounds due to the presence of the carbonaceous agent, the THEIC.

Solid-state NMR then showed unambiguously that when boric acid and coated APP are heated together at 450 °C, borophosphate is formed. As boron is in excess compared to phosphorus, the whole phosphorus reacts to yield borophosphate whereas some B_2O_3 still remains. Investigations of the residues collected at different temperatures lead to the conclusion that borophosphate appears around 250 °C. At 450 °C, only borophosphate and boron oxide remain. We concluded that the reaction yielding to borophosphate at 250 °C is a reaction between the degradation products of boric acid and coated APP. Boron oxide and the phosphoric acid formed when the additives degrade react together to yield borophosphate. As coated APP degrades into phosphoric acid between 220 and 400 °C, the reaction between boron oxide and the phosphoric acid takes place in this whole interval of temperature.

Addition of THEIC in the APP is important to mention: considering the TG curves of APP and coated APP, it is clear that coated APP degrades earlier (about 200 °C) than pure APP (about 300 °C). This allows a rapid production of phosphoric acid, and so a possible reaction at lower temperature (250 °C) between this component and boron oxide.

An efficient intumescent char has to meet different requirements such as a good mechanical resistance, rapid swelling and good adhesion to steel in order to protect the substrate in a correct manner. When combining APP and H_3BO_3 in an intumescent coating, a good mechanical resistance is observed, as borophosphate is a hard material, (hardness of 6.5/10 on the Mohs scale [36]) which also shows a good thermal stability: borophosphate begin to vaporize slowly without decomposition above 1200 °C [37]. It may be proposed that the borates provide the good structural properties of the char, whereas the phosphorus ensures the adhesion of the char on the steel [38].

4. Conclusion

In the studied intumescent formulation, two components seem to show a particularly interesting effect: boric acid and a coated ammonium polyphosphate. In a precedent paper it was shown that when these two compounds are mixed together in presence of an epoxy resin, a strong intumescent effect develops.

The aim of the study was to determine using analytical methods (TGA and solid-state NMR) the reactions occurring between these components without taking into account the resin.

It was proven in this paper that when boron is put in the same amount or in excess compared to phosphorus, a reaction takes place at about 250 °C between the degradation products of boric acid (boron oxide) and coated APP (phosphoric acid), leading to the formation of borophosphate. The synergistic agent present in the coated APP allows this reaction to take place around 250 °C. It is suggested that the formation of borophosphate is responsible for the development of a hard intumescent char when boric acid and coated APP are mixed inside the resin: the borates provide a hard and mechanically resistant char, while the presence of phosphorous allows to promote a good adhesion of the char to the steel plate.

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