

# Thermal degradation and fire performance of polysilazane-based coatings

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## ABSTRACT

This paper deals with the thermal degradation and fire performance of polysilazane (PZane) based coatings. PZanes are silicon–nitrogen backbone polymers and can be used in a wide range of applications. In this study, the fire performance of PZane coating as virgin or formulated materials were evaluated using a homemade fire testing methodology similar to the “Torch Test” fire testing method. It was shown that the performance of the PZane coating can be improved incorporating fire retardant additives. Degradation of the coating is then investigated. The mechanism of degradation of the PZane was elucidated analyzing the gas and condensed phases during the degradation. It was shown that the degradation occurs in three steps leading to the formation of  $\text{SiN}_4$  and charring at high temperature. The kinetics of degradation of the three steps of degradation was also modeled in order to predict the degradation of the PZane coating in a fire scenario.

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## 1. Introduction

In recent decades, disastrous accidents caused by damage of steel structure in fire have reminded people of the risk of fire in buildings. In particular, the collapse of the twin towers in New York, on the 11th September 2001, is one of the most important accidents demonstrating the importance of the fire protection of steel structures. Indeed, it was demonstrated that the towers did not collapse because of the impact of the planes, but because of the progressive heating of the steel which has not sufficiently been protected against fire and which reached its failure temperature rapidly [1].

Fire protection systems can be classified as non-heat absorbing (including for example intumescent protective coatings or ceramic having low thermal conductivity) and heat absorbing (including for example cementitious materials) categories [2]. One of the most used systems to protect metallic structures is intumescent paint. However, these materials are typically organic-based materials and exhibit some disadvantages. Firstly, organic additives undergo exothermic decomposition which reduces the thermal insulative value of the system. Secondly, the resulting carbonaceous char in some cases has a low structural integrity and the coating cannot withstand the mechanical stress induced by a fire. Thirdly, the coating releases organic gases which are undesirable in a closed fire environment [3]. The purpose of this work is to investigate and to

develop a new organic–inorganic hybrid system to protect steel against fire.

Polysilazane (PZane) polymers whose backbones consist of alternating Si–N bonds with pendent carbon-containing groups are widely used as precursors of silicon carbonitride ceramics. Thermal, mechanical and electrical properties of the obtained SiCN ceramics render them very suitable for high temperature applications. PZanes can for example be used as protective barrier for heat exchanger [4]. On the other hand, polysilazane have also been used as barrier on steel against oxidation [5]. Since one of the main thermal properties of PZane is its low thermal conductivity; the purpose of this paper is thus to examine the performance of polysilazane based coating for protecting steel against fire using a homemade fire testing methodology based on the “Torch Test” fire testing method. Thermal degradation of the polysilazane coating will then be studied characterizing the gas and condensed phases. Kinetic analysis of the thermal degradation will be performed in the conditions of very high heating rate in order to simulate the degradation of polysilazane with temperature conditions mimicking a fire scenario.

## 2. Experimental procedure

### 2.1. Materials

The polysilazane material used in this study is a vinyl polysilazane based material supplied by Clariant (HTT1800 grade, Fig. 1). 50 wt.% (based on the total weight) aluminium trihydroxide (ATH

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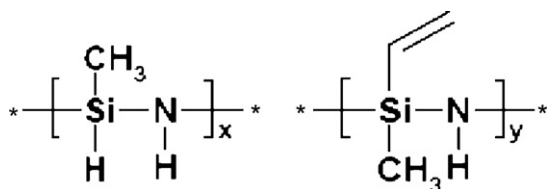


Fig. 1. Polysilazane.

from Nabaltec; grade: Apyral 40CD) was also incorporated in the polysilazane in order to enhance the fire performance of the coating. Aluminium trihydroxide has the property to be a very efficient fire retardant and not to be reacted with the polysilazane.

Coatings were applied at a thickness of  $350 \pm 40 \mu\text{m}$  on steel plates (XC38, 3 mm thick) previously coated with a primer (an epoxy resin carbomastic 15LT-A and 15LT-B from Carboline, applied at  $100 \pm 10 \mu\text{m}$ ). The coatings were cured at  $180^\circ\text{C}$  for 3 h and were then exposed to flaming performed on an IPROS flaming apparatus (50 passes with a propane flame).

Industrially, metallic structures are protected with intumescent paint (Nullfire S707). That is why a steel plate coated with intumescent paint supplied by Nullfire (England) was tested as reference.

## 2.2. Fire performance

Fire performance of the coatings was evaluated using a homemade fire testing method (Fig. 2) based on Torch Test method (American Bureau of Mines Fire Endurance Test (4), 1966). The coating is exposed to an open flame (temperature of the flame around  $1100^\circ\text{C}$ , reached in 3 s). The temperature at the back side of the plate is measured as a function of the time using a pyrometer (temperature measured in the center of the plate). The back side of the plate is previously coated with black paint (Jeltz) in order to have a constant emissivity (0.92).

## 2.3. Thermal degradation

### 2.3.1. TGA/FTIR

Gases released during the degradation of the material were analyzed using a thermo gravimetric analysis (TGA Q5000, TA Instrument) connected to a Fourier transformed infrared (FTIR) spectrometer (ThermoScientific) Nicolet iS10. The IR spectra were recorded between  $400 \text{ cm}^{-1}$  and  $4000 \text{ cm}^{-1}$ . For each sample, 15 mg of polysilazane (powder) were positioned in alumina pans. All the analyses have been carried out under nitrogen flow ( $100 \text{ mL/min}$ ).

### 2.3.2. TGA

Thermal gravimetric analysis (TGA) was carried out using a TGA Q5000 at various heating rate ( $10^\circ\text{C/min}$ ,  $100^\circ\text{C/min}$ ,  $200^\circ\text{C/min}$ ,  $300^\circ\text{C/min}$  and  $500^\circ\text{C/min}$ ) in a nitrogen flow ( $25 \text{ mL/min}$ ). For each sample, 15 mg of polysilazane (powder) were positioned in alumina pans. Both the onset (5% mass fraction loss) and peak mass loss rate have an uncertainty of  $1.5^\circ\text{C}$  ( $2\sigma$ ).

### 2.3.3. Heat treatment and characterisation of the collected residues

TGA experiments enable to define characteristic temperatures of degradation. Heat treatments were performed in tubular furnace at those temperatures under nitrogen flow for 3 h. The collected residues were then analyzed using adapted spectroscopic techniques.

The  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Advance II 400 operating at 9.4 T and equipped with 4 mm probe. Magic angle spinning (MAS) NMR spectra were acquired at a rotation frequency of 10 kHz.  $^{13}\text{C}$  NMR measurements were performed at  $100.8 \text{ MHz}$  (9.4 T) with  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization MAS. The Hartmann–Hahn relation matching condition was obtained by adjusting the power on the  $^1\text{H}$  channel for a maximum  $^{13}\text{C}$  FID signal of glycine. The  $^{29}\text{Si}$  NMR spectra were recorded on the same spectrometer as above and equipped with a 7 mm probe. Magic angle spinning (MAS) NMR spectra were acquired at a rotation frequency of 5 kHz. The reference used for  $^{29}\text{Si}$  NMR was TMS at 0 ppm. These measurements were performed with  $^1\text{H}$ - $^{29}\text{Si}$  cross-polarization MAS. A contact time of 1.5 ms was used for both  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra. For all spectra between 1024 and 12,000 scans were accumulated.

## 2.4. Kinetics analysis

Modeling and kinetics simulation of the thermal degradation were carried out from thermo gravimetric curves obtained at high heating rate ( $100^\circ\text{C/min}$ ,  $200^\circ\text{C/min}$ ,  $300^\circ\text{C/min}$  and  $500^\circ\text{C/min}$ ). Indeed, in a fire scenario the heating rate is higher than traditional heating rate used for thermo gravimetric analysis (about  $10^\circ\text{C/min}$ ). In these conditions, it is assumed that, this could simulate the polysilazane behavior in a fire scenario. At this heating rate, we recognize that mass transfer and heat transfer should occur. However these phenomena are not taken account in the kinetic analysis and in the determination of the kinetic parameters. In each case, the experiments are very repeatable and very well controlled whatever the heating rate.

Kinetic analysis and modeling of the degradation of the samples were made using an advanced thermokinetic software package developed by Netzsch Company. The principle has been discussed

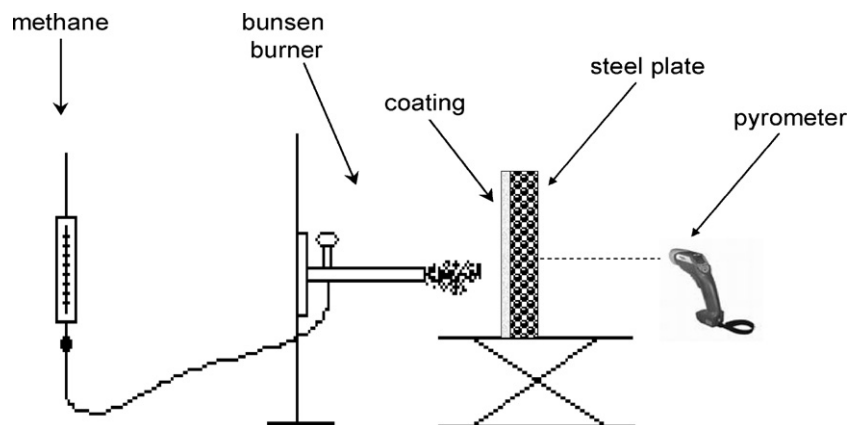


Fig. 2. Schematic representation of the Torch Test.

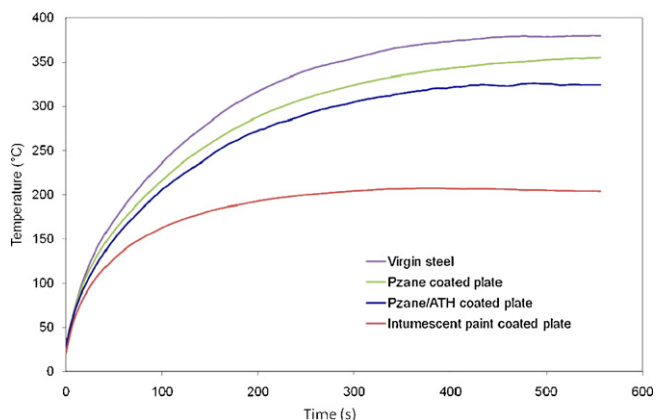


Fig. 3. Temperature profile for the virgin steel plate and for the polysilazane coatings plate.

by Opfermann [6]. For kinetic analysis, it is assumed that the material decomposes according to Eq. (1):



The rate  $d\alpha/dt$ , where  $\alpha$  is the conversion rate, is assumed to be defined by Eq. (2):

$$\frac{d\alpha}{dt} = k(T) * f(\alpha) \quad (2)$$

where  $k$  is the kinetic constant ( $k = A \exp(-E/RT)$  according to the Arrhenius law,  $A$  is the preexponential factor,  $E$  is the activation energy) and  $f(\alpha)$  is the so-called reaction model.

All reactions are assumed to be irreversible. In the case of degradation and since the evolved gases are continuously removed by the fluid flow in the TGA chamber, this is a reasonable assumption. It is also assumed that the overall reaction (Eq. (1)) is the sum of individual reaction steps (formal or true step) with constant activation energy, as generally accepted in chemistry. The model can then include competitive, independent and successive reactions. The equations are solved with multivariate kinetic analysis (determination of the parameter via a hybrid regularized Gauss–Newton method or Marquardt method) [7].

### 3. Results and discussion

#### 3.1. Fire performance

The temperature profile obtained in the Torch Test for the virgin steel plate is compared (Fig. 3) with those obtained for the pure polysilazane coating and for the formulated polysilazane coatings. It is observed in all cases that the temperature increases until around 400 s and then a steady state is reached at longer times. The temperature achieved in the steady state for the virgin plate is around 380 °C whereas that obtained for pure polysilazane and for polysilazane/ATH coated steel plate are respectively around 350 °C and 325 °C demonstrating the heat barrier properties of the coatings.

Polysilazane based coating with and without flame retardant exhibits then fire barrier properties against an open flame. In the steady state, temperature difference is 55 °C at the maximum but it remains limited compared to other classical solution such as intumescent coating (for which the temperature at the steady state is around 200 °C, corresponding to a temperature difference of 180 °C).

The picture of the sample (Fig. 4) shows a low degradation of the coating after the torch test. Even if PZane based coating does not reach the fire performance of classical intumescent coat-



Fig. 4. Sample after the torch test.

ing, it exhibits still improving properties compared to virgin steel. The objective of the study is thus, as second, to investigate the mechanism of degradation to understand the fire behavior of the material.

#### 3.2. Thermal degradation mechanism

##### 3.2.1. TGA of PZane

At first, the thermal stability of the PZane coating has been studied. TGA is shown in Fig. 5 and demonstrates an excellent thermal stability of the material.

The degradation occurs in four apparent steps, the third and fourth steps overlap. The temperature for each step where degradation rate is maximum are respectively 180 °C, 350 °C, 600 °C and 670 °C. The weight loss corresponding to each degradation is respectively 3.8%, 7.0% and 11.8%. The total weight loss at 1100 °C is only 22.6% demonstrating the excellent thermal stability of the polysilazane.

##### 3.2.2. Analysis of the gas phase

In order to determine the nature of the gases evolved during each step of the degradation previously defined, TGA coupling with a FTIR was used. The results are summarized in Table 1 whereas spectra are shown in Fig. 6. Band assignments have been done according to the literature [8].

The first step of degradation between 70 °C and 250 °C is characterized by the release of ammonia and of some oligomers of polysilazane associated to a small weight loss of 3.5 wt.%. Indeed, peaks around 950, 1625 and 3330  $\text{cm}^{-1}$  (respectively assigned to NH out of plane bending, NH in plane bending and NH stretching) are observed on the spectrum of the gases collected at 180 °C and may be attributed to ammonia. Moreover, two peaks are observed at around 1200 and 2150  $\text{cm}^{-1}$  and are assigned respectively to Si–CH<sub>3</sub> bending and Si–H stretching. We can then reasonably

Table 1

TGA data of polysilazane (\* $T_{\text{max}}$  = temperature at which degradation rate is maximum).

Step no.	Temperature range (°C)	$T_{\text{max}}$ (°C)*	Weight loss (wt.%)	Gases evolved
1	70–250	180	3.5	Oligomers, NH <sub>3</sub>
2	250–500	351	6.9	NH <sub>3</sub>
3	500–625	597	6.0	CH <sub>4</sub>
4	625–800	666	6.3	CH <sub>4</sub>

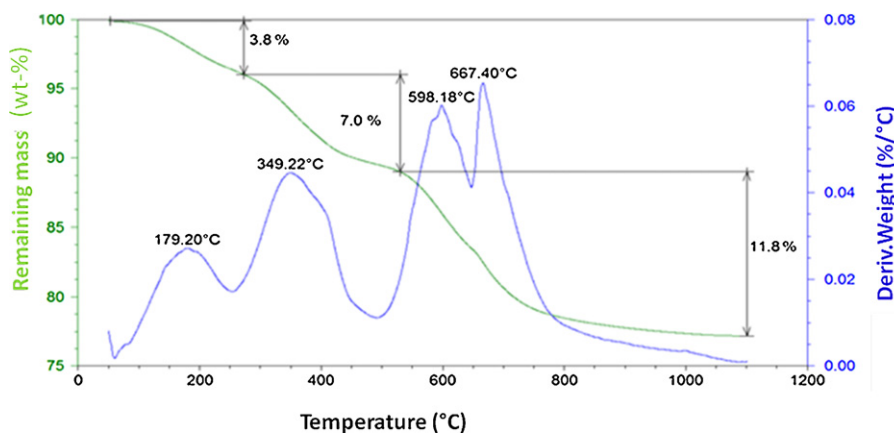


Fig. 5. TGA and DTG curves of polysilazane at 10 °C/min (N<sub>2</sub>).

assume that oligomers of PZane are evolved during this first degradation step.

During the second step, between 250 °C and 500 °C, the main gas released is the ammonia (as shown by the high intensity of the bands observed at even if oligomers of PZane are still evolved). It corresponds to a weight loss of 6.9 wt.%.

The major weight loss (12.3 wt.%) occurs at higher temperature ( $T > 500$  °C) corresponding to a released of methane (intense asymmetrical stretching in the range 2850–3200  $\text{cm}^{-1}$  and bending vibration at around 1350  $\text{cm}^{-1}$ ).

Another analysis at 100 °C/min has been carried out in order to identify the gas which evolved in a fire scenario (at high heating rate). Fig. 7 shows that the same gases are evolved during the PZane combustion and therefore it indicates that the degradation mechanism is not modified at high heating rate.

### 3.2.3. Analysis of the condensed phase

After characterizing the gases released during the pyrolysis, analysis of the condensed phase have been made in order to be able to define a degradation pathway for the PZane. Thus, residues collected after heat treatment at the previously defined characteristic temperature (HTT; heat treatment temperature) have been studied using <sup>13</sup>C and <sup>29</sup>Si solid state NMR. Peak assignments have been done according to the literature [9,10].

<sup>13</sup>C NMR spectroscopy is useful for examining the evolution of carbon in particular Csp<sub>3</sub> and Csp<sub>2</sub> hybridization and can thus show if charring occurs when a material degrades.

<sup>13</sup>C CPMAS solid state NMR spectra of polysilazane and heat treated residues are presented in Fig. 8a. It shows that at room temperature, peaks are observed between 8 ppm and –10 ppm. These peaks correspond to Si–CH<sub>3</sub> resonances which are in different environments as shown in Fig. 8b. It also appears that Si–CH<sub>n</sub>

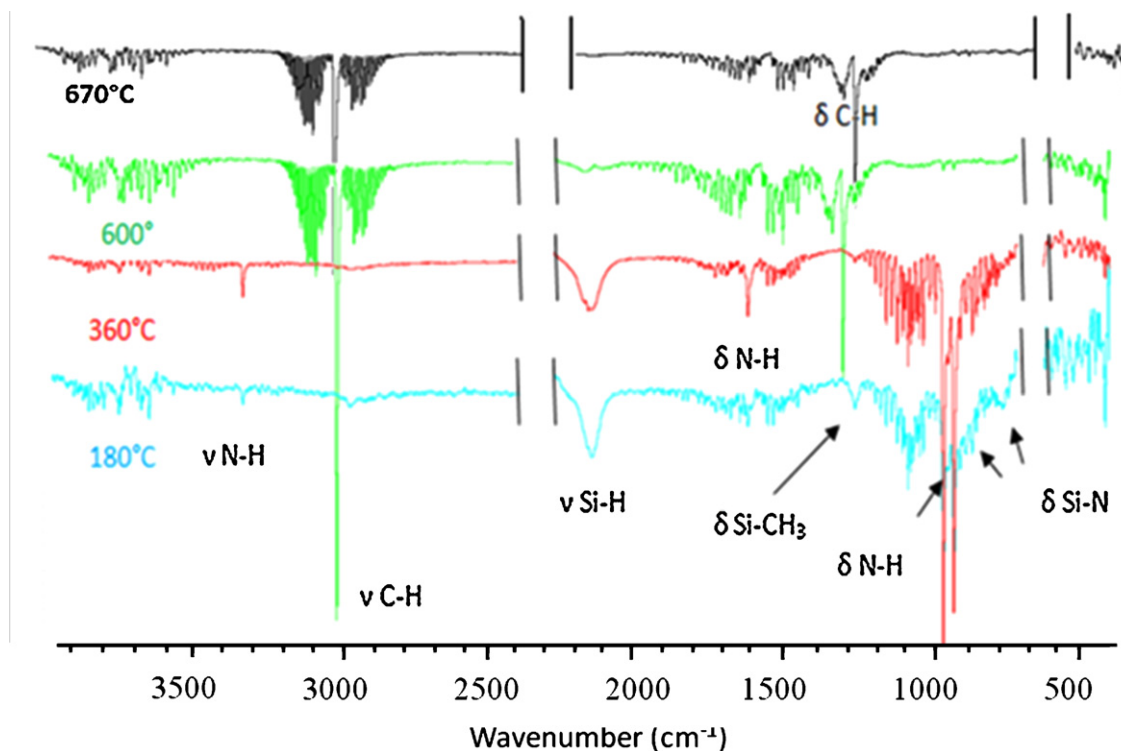


Fig. 6. IR spectra of the gas evolved during the combustion at 180 °C, 360 °C and 600 °C.

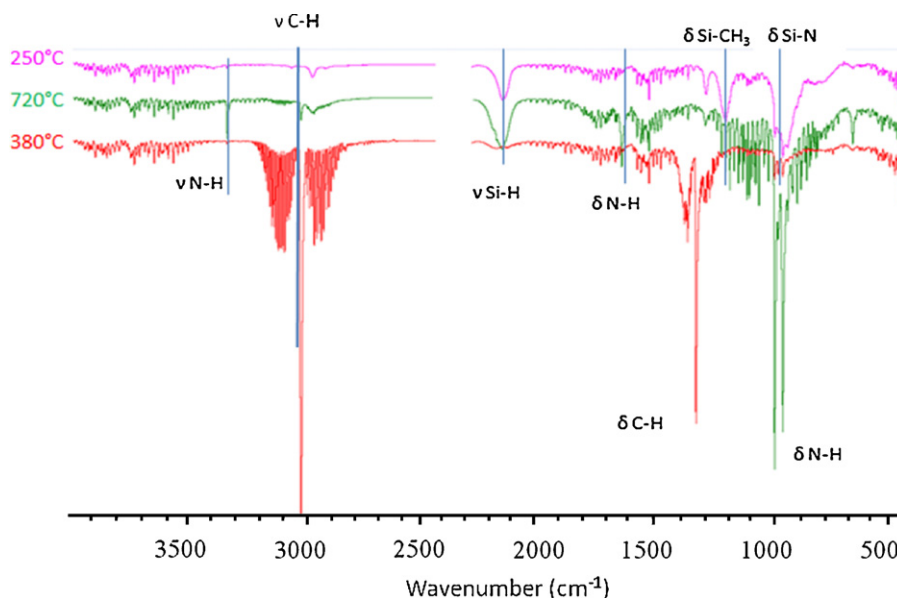


Fig. 7. IR spectra of the gas evolved during the combustion at 100 °C/min.

with  $n = 1$  or 2 are detected in the structure as demonstrated by the presence of resonance between 15 ppm and 30 ppm. The presence of such species is clearly observable when the material has been heat treated at 250 °C. It thus demonstrates that the cross-linking reaction of the vinyl carbon and/or the hydrosilation reaction are initiated at ambient temperature and proceed at higher temperature causing the formation of a tri-dimensional network within the polymer.

At higher temperature (500 °C), there is a broad peak between 135 ppm and 150 ppm corresponding to C=C bonds either in aromatic and oxidized aromatic or unsaturated systems and the residue is black. These results suggest that charring of the material occurs at high temperature.

$^{29}\text{Si}$  CP/MAS NMR spectra of the polysilazane and of its pyrolysis residues (Fig. 9) show that at room temperature, there are lots of different Si structures in PZane. The assignment of each peak is summed up in Table 2.

The  $(\text{Csp}_3)_2\text{SiN}_2$  site results to the cross-linking reaction of the vinyl function. So, it can be concluded that even if this reaction occurs at high temperature, it is initiated in the coating during its preparation. Those of  $\text{Csp}_3\text{Csp}_2\text{SiN}$  and  $\text{Csp}_3\text{SiHN}_2$  are due to the polycondensation of the Si–H and N–H bonds present in the monomer. The peak at –33 ppm corresponding to  $\text{Csp}_3\text{Csp}_2\text{SiHN}$  is due to the end of the chain of the PZane. It is important to underline that the polymer is also partially hydrolyzed and/or oxidized. Indeed,  $T_1$ ,  $T_2$  and  $T_3$  structures are detected at –49 ppm, –60 ppm and –68 ppm respectively. These structures are shown in Fig. 10.

At 250 °C, there is the appearing of  $\text{SiN}_3$ . At high temperature (500 °C),  $\text{SiN}_4$  environment appears at –45 ppm and only  $(\text{Csp}_3)_2\text{SiN}_2$  and  $\text{Csp}_3\text{SiN}_3$  sites are present with a resonance at –8 ppm and –20 ppm respectively.

### 3.2.4. Thermal degradation mechanism

After analyzing the condensed and gas phase during the degradation and characterizing each step of degradation, the polysilazane thermal degradation mechanism can be established.

At room temperature, the presence of  $(\text{Csp}_3)_2\text{SiN}_2$  and  $\text{Si-CH}_n$  with  $n = 1$  or 2 clearly observed in  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra could be attributed to the cross-linking reaction and to the hydrosilation reaction (Fig. 11) which occurs during the polymerization and condensation of the PZane.

For  $T_{\text{amb}} < T < 180$  °C, according to the gas phase analysis, oligomers of polysilazane are released. Exchange of Si–N bonds could lead to the formation of silazane oligomers having the same structural units as the precursor, whereas the exchange between Si–N and Si–H bonds could lead to volatile silanes (Fig. 12).

Between 250 °C <  $T$  < 450 °C, cross-linking reactions occur. Most of the vinyl functions have polymerized as described in Fig. 13 leading to the formation of a tri-dimensional network. Moreover, there are formation of  $\text{SiN}_3$  structures (according to  $^{29}\text{Si}$  NMR spectra) due to the polycondensation of remaining Si–H and N–H bonds. This step is also characterized by the released of ammonia due to the reaction of transamination (Fig. 13).

For  $T > 450$  °C, mineralization of the PZane occurs. This step is characterized by the released of methane, the formation of  $\text{SiN}_4$  sites (clearly observable in  $^{29}\text{Si}$  NMR spectrum) and charring (broad peak observed between 135 ppm and 150 ppm in the  $^{13}\text{C}$  NMR spectrum of PZane heat treated at 500 °C). The evolution of methane could be explained by the following reaction (Fig. 14).

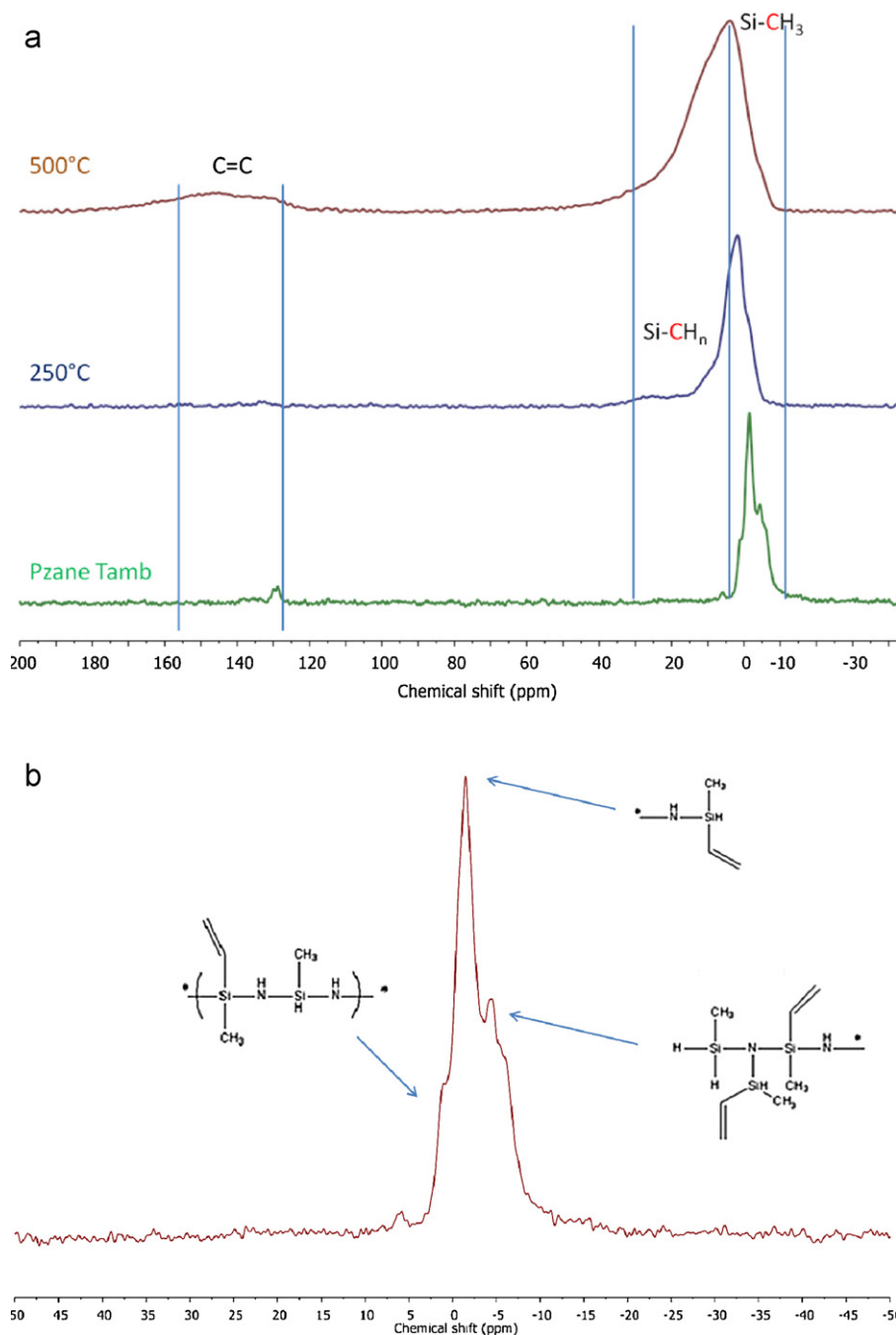
### 3.2.5. Kinetic analysis of the thermal degradation of PZane coating

Kinetic analysis could be a useful tool in order to better understand the degradation mechanism of materials and also to predict its behavior in different fire scenario [11]. That is the reason why, kinetic analysis of the thermal degradation of the PZane coating was carried out.

TG curves of polysilazane for different heating rate are presented in Fig. 15. For this study, high heating rate were used (from 100 °C/min to 500 °C/min) in order to obtain kinetic parameters in conditions as much as possible close to those of a fire. Another experiment has been performed at 10 °C/min (Fig. 5) as we did at high heating rate in order to check if the model can be extrapolated to low heating ramp. A similar total weight loss is observed

Table 2  
Assignment of  $^{29}\text{Si}$  NMR spectra of the polysilazane at room temperature.

Chemical shift (ppm)	Site
–8	$(\text{Csp}_3)_2\text{SiN}_2$
–18	$\text{Csp}_3\text{Csp}_2\text{SiN}_2$
–24	$\text{Csp}_3\text{SiHN}_2$
–33	$\text{Csp}_3\text{Csp}_2\text{SiHN}$



**Fig. 8.** (a)  $^{13}\text{C}$  CP/MAS NMR spectra of the polysilazane and of its residues at different HTT (250°C and 500°C) and (b) zoom of the Pzane  $^{13}\text{C}$  CP/MAS NMR spectrum at ambient temperature in chemical shift range [60; -60 ppm].

whatever the heating rate (around 25 wt.%) and the shape of the curves suggests a pyrolytic degradation occurring in several step, as observed previously when a lower heating rate was used.

Before starting any fitting procedure to model the degradation of PZane, it is necessary to define a model (combination of reactions) and to preset starting values for the kinetic parameters. A convenient approach is to use model-free analysis as a preliminary step of the kinetic analysis. A model-free analysis, such as the well-known Friedman analysis [12], provides the plot of the activation energy versus the fractional weight loss (Fig. 16).

This analysis reveals that the activation energy is not constant, but increases from 50 to 200 kJ/mol. This indicates that the degradation does not take place as a one-step reaction but as multistep reactions, probably as due to consecutive reactions. In order to

estimate the number of the step which occurs in the degradation, derivative TG curve obtained at 200°C/min has been calculated and is reported in Fig. 17. This curve exhibits three maxima and as a consequence, it will be assumed that for high heating rates, the thermal degradation occurs in three apparent steps (four steps were observed when TG analysis was carried out at 10°C/min).

The thermal degradation of the polysilazane has then been modeled using three consecutive step ( $A \rightarrow B \rightarrow C \rightarrow D$ ) with Avrami–Erofeev functions (they describe an  $n$ -dimensional nucleation/nucleus growth according to Avrami–Erofeev [13]  $f(\alpha) = n(1 - \alpha)^{n-1} [-\ln(1 - \alpha)]^{1-1/n}$ ). Among the classical types of global kinetic models, Avrami–Erofeev function is used to describe polymer degradation. Here, the Avrami–Erofeev function was chosen because it gave the highest quality of fit, compared to other degra-

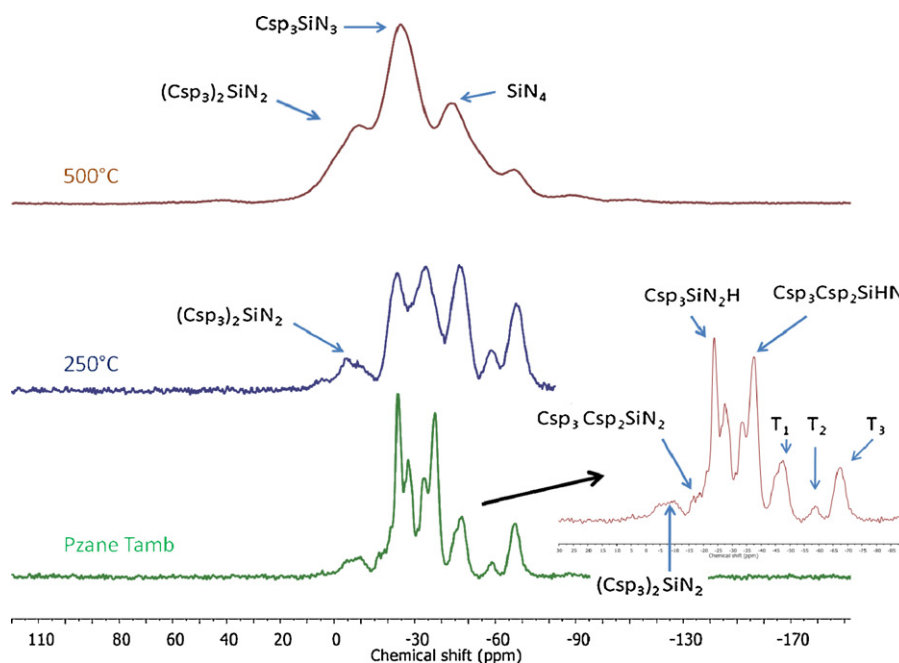


Fig. 9.  $^{29}\text{Si}$  CP/MAS NMR spectra of the polysilazane and of its residues at different HTT (250 °C and 500 °C).

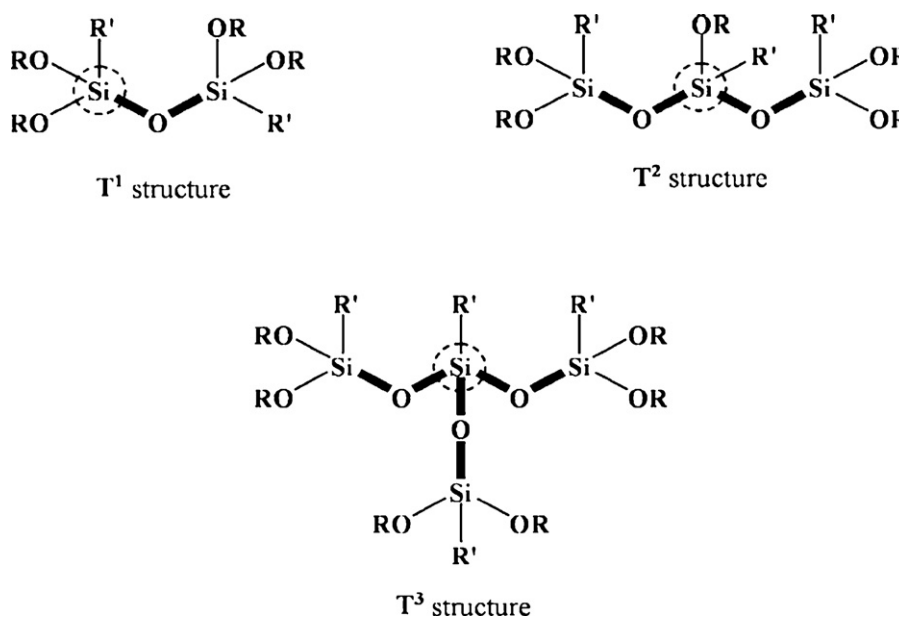


Fig. 10. Schematic presentation of  $T^i$  silane structures.

degradation functions. Indeed, the defined model fits the experimental TGA curves very well (Fig. 18). The associated kinetic parameters are presented in Table 3. All the kinetics parameters have been calculated for high heating rate. Fig. 19 shows the modeling at 10 °C/min for testing the robustness of the model. It shows that

**Table 3**  
Kinetics parameter for each thermal degradation steps.

Step	$\log(A)$ ( $A$ in $\text{s}^{-1}$ )	$E$ (kJ/mol)	Dimension $n$
Released of oligomer	2.3	40.7	0.9
Formation of a tri-dimensional network	7.0	106.6	0.7
Formation of $\text{SiN}_4$ and charring	7.9	172.1	0.4

for the low heating rate the simulated values do not fit very well the experimental values. It can be explained by the very heating rates used in the TGA experiments and 15 mg samples of a poorly conducting material cannot be heated in a uniform fashion. The degradation processes will be then controlled by either heat transfer inside the sample or thermal resistance between the sample and heating element. As conclusion our modeling approach for the thermal degradation of PZane can only be used for high heating rate as occurring in fire conditions.

These values show that all the degradation steps occur in one dimension and the formation of  $\text{SiN}_4$  and charring require more energy than the released of oligomers and the formation of a tri-dimensional network.

The goal of the kinetic analysis was not only to study the degradation of the PZane but also to predict its behavior in various fire

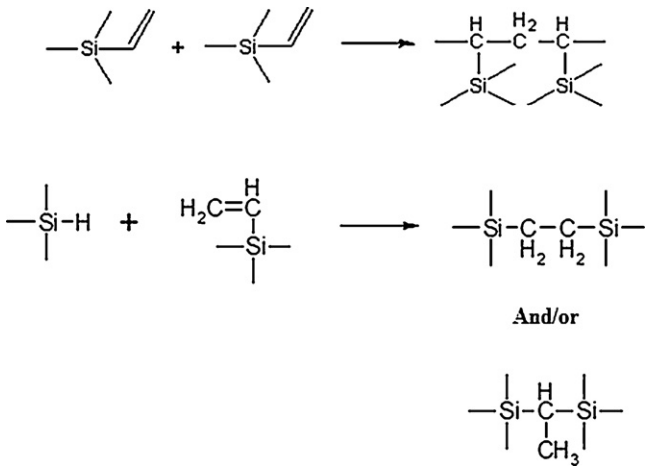


Fig. 11. Cross-linking reaction and hydrosilation reaction of silazane monomers.

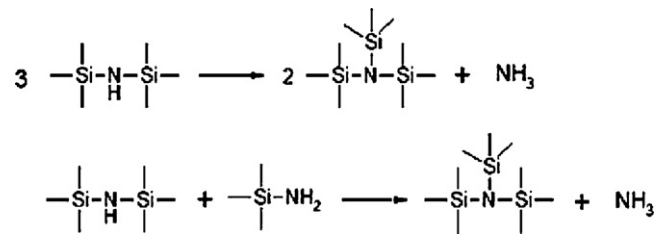


Fig. 13. Reaction of transamination.

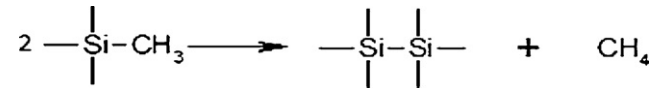


Fig. 14. Reaction leading to the emission of methane.

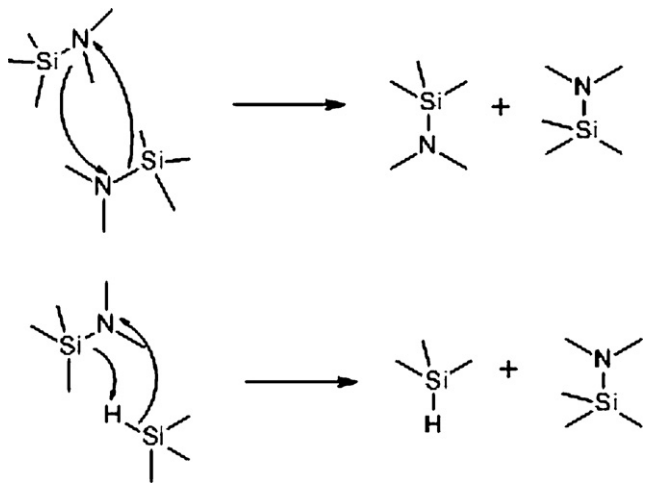


Fig. 12. Reactions leading to the released of PZane oligomers and silane.

scenarios. Since the objective of our study is to develop fire protective coating for steel structure, ISO 834 curve was selected as fire scenario. This curve describes the temperature development of a cellulosic fire based on the burning rate of the materials found in

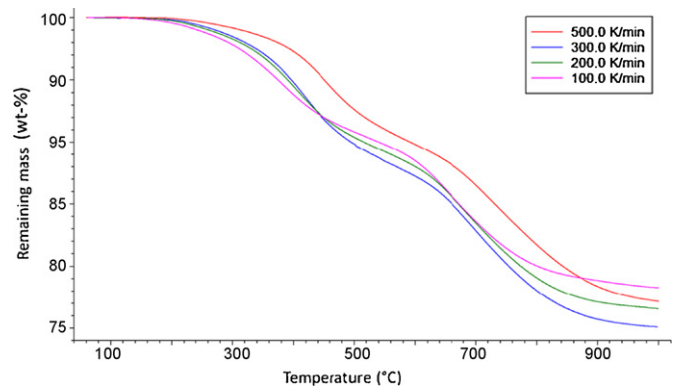


Fig. 15. TG curves of polysilazane at high heating rate.

general building materials and contents. Results are presented in Fig. 20.

This simulated curve shows that the polysilazane should be very stable in the case of such a fire scenario. Degradation mainly occurs during the first 12 min leading to a residual weight loss of 74% after 1 h exposure to a fire.

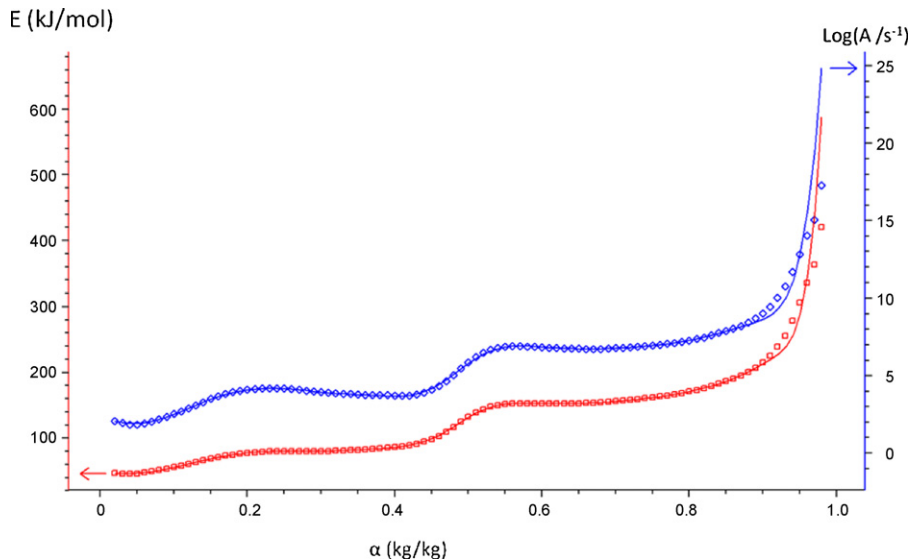


Fig. 16. Activation energies of polysilazane versus fractional mass loss determined using the Friedman analysis.



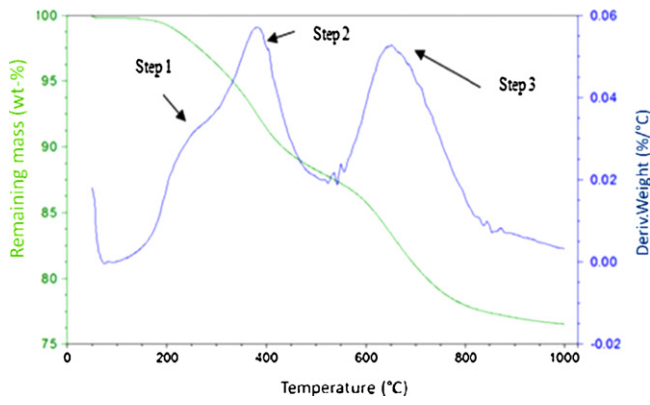


Fig. 17. TG and DTG curves of polysilazane at 200 °C/min (N<sub>2</sub> flow).

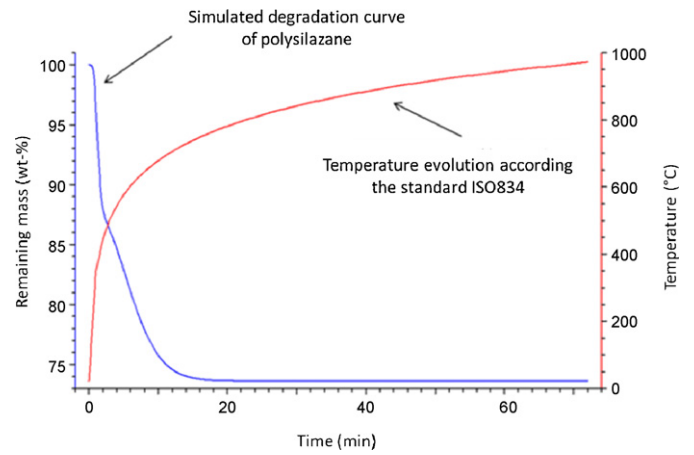


Fig. 20. Simulated degradation of polysilazane in a fire scenario (standard ISO834).

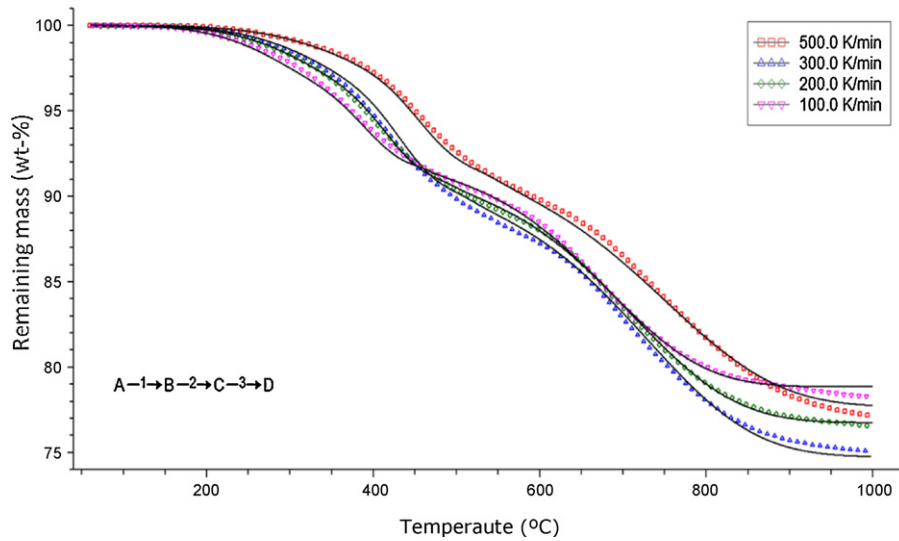


Fig. 18. Experimental (dotted) and simulated (line) TG curve of polysilazane (N<sub>2</sub> flow).

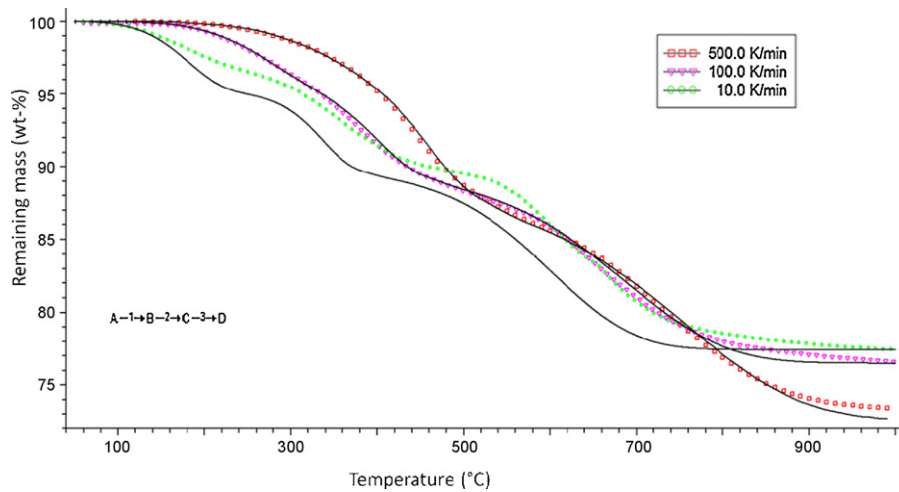


Fig. 19. Robustness test for kinetic analysis.

#### 4. Conclusion

This paper has investigated the thermal degradation and fire performance of polysilazane based coatings. The fire performance of polysilazane coating has been evaluated using a homemade fire test based on the Torch test. This shows that the performance of the polysilazane coating can be improved incorporating some fire retardant such as aluminium trihydroxide. Other additives such as blowing agents could also enhance this fire performance and further investigations are currently carried out in our laboratory.

The thermal degradation mechanism was also investigated and has been elucidated analyzing the gas and condensed phase during the degradation; it was shown that the degradation occurs in three steps during a fire scenario leading to the formation of SiN<sub>4</sub> and charring at high temperature.

Finally, each steps of the degradation have been characterized by kinetics modeling at high heating rate in order to predict the thermal degradation behavior of the coating in a fire scenario. The degradation was modeled using a three consecutive steps model in one dimension with Avrami–Erofeev functions. It was shown that PZane is very stable since the residual mass obtained after 1 h in ISO834 conditions is around 76% [8].

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