



Determination of physicochemical properties for silicone composite and its thermal numerical simulation

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Abstract

Silicone-based composites material found a large use in the aerospace industry to protect wall structures from severe heating. To determine experimentally the thermophysical properties (λ , ρ , C_p) and the kinetic triplet (E_a , A , n) from ambient temperature to 1000°C, dedicated experimental apparatus are used. An experimental procedure has been carried out on a generic silicone-based composite, it consists of a silicone matrix with short carbon fibres and silicon carbide powder. First, thermogravimetric analysis has been conducted on the material at different heating rate and confirming the complex thermal degradation, thus under inert atmosphere, the weight of the material decreases up to 28.8%. From these results, a kinetic mechanism degradation and a methodology for a correct estimation of the triplet kinetic parameters are proposed. Several apparatuses have been used to determine the thermophysical properties such as Calvet calorimeter, Differential Scanning Calorimetry, dilatometer and laser flash analysis, from this result the thermal conductivity is estimated. Once the properties are determined, the measured data has been implemented in a finite element 1D approach, showing the efficiency of the generic silicone-based composite as a thermal barrier.

Keywords: Kinetic analysis, Flash diffusivity, Dilatometry, Differential scanning calorimetry, thermal behaviour modelling

Nomenclature

Latin

A – Activation energy
 C_p – Specific heat
 E_a – Pre-exponential factor
 k – Coefficient of thermal expansion
 m – Mass
 n – Order of reaction
 Q – Heat flux
 R – Gas constant
 T – Temperature

t – Time

V – Volume

Greek

α – Degree of reaction
 λ – Thermal conductivity
 ρ – Density

Subscripts

0 – initial
 f – final

1. Introduction

During the atmospheric re-entry of a spacecraft, the spacecraft's structures are subjected to severe thermal conditions and high temperatures (at a level where material degradation cannot be neglected) [1,2]. Such severe environment requires a thermal protection system (TPS) to guarantee safe operations, by preventing a structure failure due to the penetration of the high heat fluxes in the vehicle's structure.

Ablative Thermal Protections (ATP) materials have found a large interest in the aerospace industry to protect the structure against severe thermal conditions [3-4]. Indeed, contrary to metal structures such as steel or titanium alloys, these materials are suitable for absorbing the heat flux through complex

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physico-chemical phenomena. During a severe heating, their degradation includes several effects, such as in-depth material pyrolysis and surface ablation [5].

Because of the difficulty in carrying experiments on ATP materials at severe thermal conditions, numerical simulation represents a useful tool for the evaluation of their shielding performance and generate positive impacts such as the reduction of cost and of weight such as the increase in the lifetime of the material [6]. However, to accurately reproduce the complex physico-chemical phenomena during a severe heating, numerical models require several thermophysical and kinetic properties as input parameters. For instance, thermophysical properties such as the specific heat (C_p), the thermal conductivity (λ) and the density (ρ) are implemented in numerical models as functions of temperature. Moreover, the kinetic triplet of the thermal degradation, which are the pre-exponential factor (A), the activation energy (E_a) and the order of reaction (n), are introduced as constant parameters.

Consequently, the creation of a complete properties database represents a large issue, especially for Thermal Protection Systems (TPS) materials in aerospace applications. Methods for determining input parameters in numerical models can be divided into two approaches [7]: indirect and direct. The first approach is to evaluate material properties numerically from experimental data collected in a medium-scale tests. A numerical model is coupled to an optimization algorithm and used to simulate the experimental data. Then, the input parameters are adjusted to provide the best possible agreement between the experimental test and the numerical model. It is important to note that these properties are not necessarily fully "physical" because they may also account for phenomena or scales which are not explicitly considered numerically. Moreover, this approach is limited to a small number of parameters and the results are highly sensitive to the accuracy of the experimental data. The second approach consists of using dedicated experimental apparatus to directly measure each thermophysical or kinetic property.

Among TPS materials, silicone rubber composites are robust candidates for thermal insulation due to their low thermal conductivity and high thermal stability [8-11]. This kind of material has been already used for thermal protection management of spacecraft, thanks to its particularity of being directly processed in a liquid state at room temperature [8]. When the silicone rubber composite is exposed to severe external heat flux like the one of the combustion chamber gas, the material is transformed and removed by two main phenomena [12]. The first one is the pyrolysis phenomenon, which refers to the thermochemical degradation of the material when a certain temperature level is reached. This phenomenon is associated to the degradation kinetics of the material which involves the production of gaseous species and a solid char residue. As the material decomposes, the pyrolysis front progresses within the material, leaving behind a char layer. Consequently, the silicone rubber composite is composed of two parts, a virgin material and a charred material separated by a pyrolysis zone. Meanwhile, the second phenomenon occurs at the surface of the material and causes the removal of the char layer. This degradation is commonly called ablation and can be caused by chemical reactions or mechanical degradation, such as oxidation or erosion (due to high speed flow interacting with the material surface).

In the light of the above, the determination of their thermo-physical properties can be very challenging at high temperatures [13]. Furthermore, within the same material, strong heterogeneity can be found due to the inherent variability of the manufacturing process or the formulation of the material, so the blind use of literature data as inputs for numerical models might represents a critical aspect. Therefore, the accurate determination of the thermophysical properties allows numerical models to achieve predictive calculations, providing a cost-effective alternative by reducing the required number of large-scale tests.

In the same underlying idea, the present study aims at first to determine experimentally the thermophysical properties (λ , ρ , C_p) and the kinetic triplet (E_a , A , n) in a large range of temperatures. An experimental procedure has been carried out on a generic silicone-based composite with dedicated experimental apparatus. Finally, the measured properties are implemented in a numerical tool and used to simulate the expected behaviour of the material along a generic hypersonic re-entry trajectory, taken from the literature.

2. Materials and methods

The generic composite material investigated here consists of short carbon fibres and silicon carbide powder introduced into a silicone matrix. To investigate the thermal stability and degradation of this manufactured silicone-based composite, Thermo-Gravimetric Analysis (TGA) are conducted with SDT Q600 TA Instruments which consists in monitoring the sample mass-loss evolution when the material is subjected to a specific heating program. This technique gives information on the decomposition pathway of the material and allows to deduce the decomposition mechanisms. A Netzsch STA 449 F3 apparatus is used to evaluate the specific heat of the composite as a function of temperature under nitrogen atmosphere and atmospheric pressure. To measure the evolution of volume of the composite as a function of temperature, a dilatometer (TMA 402-F3 Hyperion) is also employed under nitrogen atmosphere and a heating rate of 5°C/min. Then, the density variation is calculated according to the temperature. Concerning the measurement of thermal diffusivity, the flash method was used, allowing the calculation of the thermal conductivity. Thermal diffusivity of the samples is measured between room temperature and 1000°C under inert atmosphere with a heating rate of 5°C/min. The specific heat and the density are determined from the ambient temperature up to 1000°C.

2.1. Material and elaboration

A generic silicone-based composites, is considered in this study. The silicone rubber matrix was prepared from RTV630 [14], which means Room Temperature Vulcanization of silicone rubber, the latter is a room temperature curing silicone elastomer [8]. RTV630 consists of a two-part kit and it has the particularity of being easily injectable into a mould. The choice of a silicone matrix is based on the nature of the char residue. Indeed, when silicone matrix is subjected to a high thermal flux, the pyrolysis of the material results in the production of a solid silicon carbide residue. The latter has the advantage of being a refractory material with good mechanical strength which can withstand extreme thermal conditions [15-16], extending the life of the TPS.

Then, the solid fillers are composed of carbon fibre and silicon carbide powder. The use of carbon is interesting for its high mechanical strength, low density and chemical inertia in non-oxidizing environments. Carbon fibres are thus commonly used in TPS material. In this moulding material, the carbon fibres have been chosen with a length of 6 mm. Finally, the powder used for this material consist of silicon carbide, as said before, this material has interesting refractory properties.

The composite has been prepared by blending first the two parts of the silicone resin, silicon carbide powders and carbon fibres in a Z-blade mixing systems (Mixer GUITTARD®) with a mixing speed between 10 rpm and 50 rpm, to ensure that the fillers are homogeneously impregnated. The latter is also equipped with a water-cooling system, so that the mixing temperature is between 5°C and 15°C. To avoid air entrapment and bubbles in the finished mould, the mixed silicone rubbers should be vacuumed during the blending (-0.7 bar). The Fig. 1 illustrates a schematic overview of the reduced pressure mixing apparatus used for sample preparation.

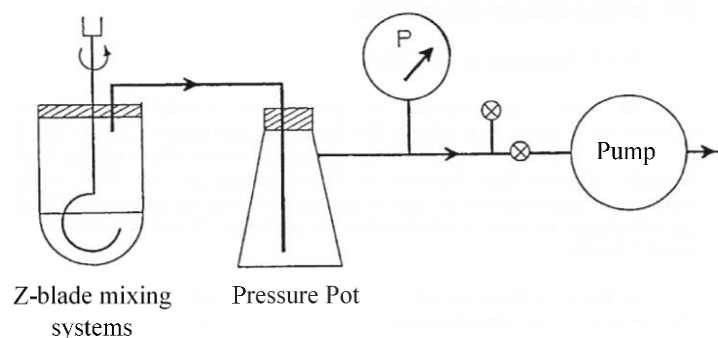


Fig. 1 Schematic of the reduced pressure mixing apparatus

The prepared mixed can be moulded using compression or compression-transfer molding techniques. During the injection, the prepared mixed were cured in a steel mold at a temperature of 60°C during 6 hours with an injection pressure of 30 bars. In this study, the generic silicone-based composite is prepared with a specific carbon fibres and silicon carbide powder weight proportion as show in the Table 1.

Table 1. Composition of the silicone-based composites studied

Components	PBW	weight proportion (%)
RTV 630 (Part A)	100	73
RTV 630 (Part B)	10	7.3
Carbon fibers	13	9.6
Silicon carbide powder	13	9,6

PBW: Parts by weight

2.2. Kinetic parameter determination using TGA

As mentioned in the introduction, to investigate the thermal stability and degradation of the manufactured silicone-based composites, thermogravimetric measurements were conducted with an SDT Q600 TA Instruments. Thermogravimetric apparatus represents a useful tool for the study of thermal degradation, it provides quantitative and qualitative results on the chemical reactivity of a solid material. This equipment consisted of a platinum crucible paired with a thermocouple type R (Platinum/Platinum-Rhodium) and an electronically controlled balance, allowing to record the evolution of the weight of a sample as it is heated under a specific heating program and composition atmosphere. Thus, TGA typically provides the mass (m) and the mass-loss rate (dm/dt) of the sample at a corresponding temperature.

In this work, specimens were tested under inert conditions (argon) at atmospheric pressure from room temperature to 1000°C followed by an isothermal phase of 15 minutes, at several heating rates of 5, 10, 15, 30 and 40°C/min. The samples for the TGA are directly cut from a virgin plate (see Fig. 2) and masses between 47.99-58.93 mg are considered in this experiment. The initial masses of the samples for the TG experiments are reported in the Table 2 for each heating rates program. Thus, small sample's masses are considered in this study, to limit temperature gradients inside the samples during the experimental tests.

**Fig. 2** Picture of the plate and the virgin samples used for the TGA**Table 2.** Initial masses of the sample for TGA

Heating rates (°C/min)	Mass sample (mg)
5	47,99
10	49,78
15	48,46
30	58,93
40	49,25

Modelling the thermal degradation of a material requires to accurately knowing all the mechanism degradation of the matter, which can be problematic for composite materials. In fact, due to their heterogeneity, these kinds of materials are associated with complex and multi-step chemical reaction. Therefore, simplifications are carried out in order to investigate the thermal degradation because of the complexity of the physical and chemical reactions inside the material.

A comprehensible reaction pathway associated with a simplified decomposition kinetic model can be proposed to explain matter transformation. In this study, the chemical reactions of the composite material are partially unknown, therefore, a decomposition kinetic model of the mechanism process is proposed. In the literature, several approaches are available and can be divided into two categories: model-free analysis and model-based analysis [17].

Model-free analysis [18] assumes that the decomposition rate of the solid material can be described by only one kinetic equation based on the Arrhenius equation given as

$$\frac{d\alpha}{dt} = A(\alpha)f(\alpha)\exp\left(-\frac{E(\alpha)}{RT}\right) \quad (1)$$

where α is the degree of reaction, $A(\alpha)$ is the pre-exponential factor depending on the conversion α , $f(\alpha)$ is the reaction model and $E(\alpha)$ is the activation energy. The degree of reaction α will vary between 0 and 1, corresponding respectively to the virgin state and char state of the material. In TGA experiments, α is defined as

$$\alpha = \frac{m(t) - m_0}{m_f - m_0} \quad (2)$$

where m is the mass of the sample according to the time t , m_0 and m_f are respectively the initial and final mass of the sample.

Using the achieved experimental data, the kinetic parameters triplet (activation energy, pre-exponential factor and reaction model) can be determined by means of different model-free methods such as Friedman analysis or Ozawa-Flynn-Wall analysis [19]. However, a correct estimation of this kinetic triplet is possible when the degradation process can be described by a succession of isolated single-steps reaction. In the light of this, a more generalist method has been implemented which is called model-based method.

The approach of the model-based analysis assumes that a complex kinetic degradation consists of several independently steps which are described by their own kinetic equation. The kinetic equation for each i step is described by a single Arrhenius law which is defined in the Eq. 3.

$$\frac{d\alpha_i}{dt} = A_i f_i(\alpha_i) \exp\left(-\frac{E_i}{RT}\right) \quad (3)$$

In this equation, the pre-exponential factor A_i , the reaction model $f_i(\alpha_i)$ and the activation energy E_i for each i step of the thermal degradation are assumed constant during the reaction process. Consequently, in this method the total material degradation is described a sum of single steps reactions.

These two methods differ in their approaches to modelling complex thermal degradation. For the model-free method, the degradation kinetics is described through a single Arrhenius law whose parameters depend on the state of progress of the reaction. In the literature, this type of approach has shown limitations for complex kinetics, therefore, a model-based approach is used. From the TGA curves, a kinetic mechanism formed by several apparent reactions is proposed. Once a kinetic mechanism is proposed, the main kinetic parameters of this decomposition kinetic model are estimated by an optimization technique such as least mean squares method. This optimization technique will attempt to find the best fit between experimental and numerical weight loss curve.

2.3. Thermophysical properties measurement

This subsection describes the measurement techniques and the different apparatus used for the determination of the material properties. The specific heat is measured from the ambient temperature up to 1000°C by using a Differential Scanning Calorimetry (DSC), plus a Calvet calorimeter. The density variation is calculated according to the temperature by using a dilatometer device. Finally, the determination of the thermal diffusivity is carried out by using the flash method, followed by calculation of the thermal conductivity.

The specific heat is measured by using two different apparatus to ensure a good representation of the value between ambient temperature and 1000°C. First, a Calvet calorimeter is used to measure the specific heat of the silicone composite-based material at ambient temperature and 150°C. This initial measurement is carried out by using a Setaram C80II three dimensional Calvet calorimeter [20-21]. During the experiment, an initial isotherm of 5.6 hours at a temperature of 1 °C below the target value is set. Then a ramp with a heating rate of 0.05 °C/min is applied to reach 1 °C above the target temperature, and finally followed by an isotherm step of 3.9 hours. The specific heat at the target temperature is defined in the Eq. 4.

$$\bar{C}_p = \frac{Q_{sample} - Q_0}{m_{sample} \times \Delta T} \quad (4)$$

where Q_{sample} is the heat flow rate into the sample, Q_0 is the heat exchange obtained during the blank experiment, m_{sample} is the mass of the sample and ΔT the temperature interval (in this study ΔT is equal to 2°C).

This method allows to obtain by direct measurement the specific heat of the material, however for higher temperatures a DSC must be used. In this study, DSC experiments are carried out by using a Netzsch STA 449 F3 from ambient to 1000°C. The conventional three-step technique for the determination of the heat capacity is used in this study. The specific heat capacity C_p of the sample is calculated by equalizing the heat flux absorbed by the sample with the one absorbed by a calibration material using:

$$C_p = C_{p,ref} \frac{m_{ref} \times (\Phi_{sample} - \Phi_0)}{m_{sample} \times (\Phi_{ref} - \Phi_0)} \quad (5)$$

where Φ_{sample} , Φ_{ref} and Φ_0 are, respectively, the measured heat flux for the sample, the calibration material and the blank experiment, m_{sample} and m_{ref} are, respectively, the mass for the sample and the calibration material. During this experiment, the test has been carried out under nitrogen atmosphere from ambient to 1500°C with a heating rate of 20°C/min. The samples for the calorimeter experiment and the DSC experiment are extracted from two different locations of the virgin plate with a mass of, respectively, 4.43 g and 38.93 mg (see Fig. 3). The samples used for the calorimeter measure 5*5*55 mm, while for the DSC experiments, samples with a diameter of 4 mm and a thickness of 1 mm have been used.

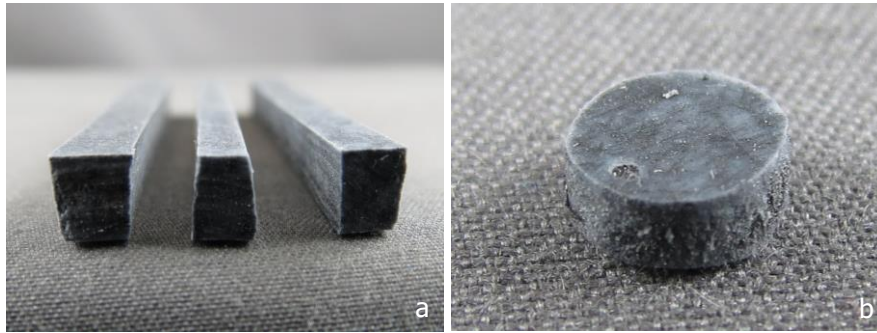


Fig. 3 Calorimeter sample (a) and DSC sample (b)

The density variation is calculated by using a TMA 402-F3 hyperion dilatometry apparatus. This measurement is based on measuring the volume change of the sample during its heating. The sample is submitted to a heating rate of 5 °C/min and tested from ambient temperature to 1000 °C under nitrogen atmosphere. The variation of volume as a function of temperature is recorded during this experiment and the coefficient of thermal expansion k is measured using the following relation:

$$k = \frac{1}{V_0} \frac{dV}{dT} \quad (6)$$

where V_0 is the sample volume at the temperature room and V is the sample volume at the temperature T . Finally, the density variation according to the temperature T is calculated by means of the Eq. (7) with m_s the mass of the sample estimated during the thermogravimetric analysis.

$$\rho = \frac{m_s}{V_0(1 + kdT)} \quad (7)$$

During the dilatometer experiments, the volume variation of the samples has been measured along the thickness and the tests were performed twice to ensure the repeatability of the results.

The thermal conductivity λ is directly calculated from the above measurements (i.e. density ρ and heat capacity C_p) and the thermal diffusivity α [22]. The latter is determined by using the flash diffusivity method. This method consists of applying a Dirac impulse of energy on the front face of the sample, then recording the temperature variations on the back face as a function of time. The resulting

temperature curve obtained is called a thermogram. Different techniques can be found in the literature for the estimation of the flash diffusivity from the obtained thermogram. In this study, the partial temporal moments method is used [22]. The thermal conductivity λ is then calculated as:

$$\lambda = \alpha \cdot \rho \cdot C_p \quad (8)$$

As said before, the silicone-based composite is subjected to thermochemical degradation when a certain temperature level is reached. This phenomenon is called pyrolysis and results in the production of gaseous species. During the flash diffusivity experiment, the emission of volatiles can pollute the optical system and make it difficult to measure the temperature variations on the back face. To this end, the thermal diffusivity is measured before and after the thermochemical decomposition of the studied material. Therefore, the test has been carried out on four samples directly extracted from different locations of the virgin plate, two samples have been used before the thermochemical decomposition of the composite (see Fig. 4a), whereas the two others have been thermally degraded before the test for the determination of thermal diffusivity at high temperature (see Fig. 4b). The latter are thus thermally degraded by subjecting the sample to a temperature above the pyrolysis phenomena (800°C) for 2 hours under inert atmosphere.



Fig. 4 Thermal diffusivity sample at virgin state (a) and pyrolyze state (b)

3. Numerical simulation

A numerical model is implemented to predict the thermal behaviour of the studied generic silicone-based composite. To this end, the measured properties are implemented in a numerical tool and used to simulate the expected thermal behaviour of the material. The numerical simulation is performed using the finite element SAMCEF, a software which provides structural and heat transfer analysis. In this work, the Amaryllis modulus is used to model the in-depth heat transfer conduction, as well as the decomposition of the silicone matrix.

The test case simulation is a simplified 1D problem from the literature [23], which was initially used for code-to-code comparison with a theoretical ablative composite (TACOT) [24]. This numerical test consists of a sample with a thickness of 50 mm. At the front face ($x=0$ mm), a convective boundary condition of 450 kW/m² for 1 min at atmospheric pressure has been assigned at the top of the computational domain. The back and side faces of the computational domain are set as adiabatic (Fig. 5). To investigate the thermal response of the silicone-based material, the temporal evolutions of the temperature profiles are monitored at five points (from T1 to T5) within the which correspond to the positions relative to the heated surface (1, 2, 4, 8 and 16 mm).

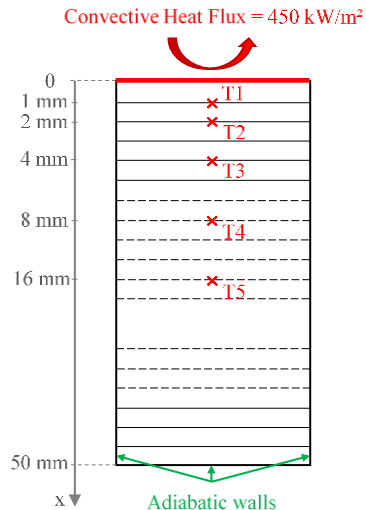


Fig. 5 Schematic overview of the computational domain

4. Results and discussion

4.1. Experimental characterization

As indicated previously, TGA experiments have been performed under inert atmosphere to obtain the mass variation of the generic silicone-based composite for different heating rates (5, 10, 15, 30, 40°C/min). The results of the weight loss (defined as the ratio between the instantaneous mass and the initial mass) and its derivative are reported on the Fig. 6.

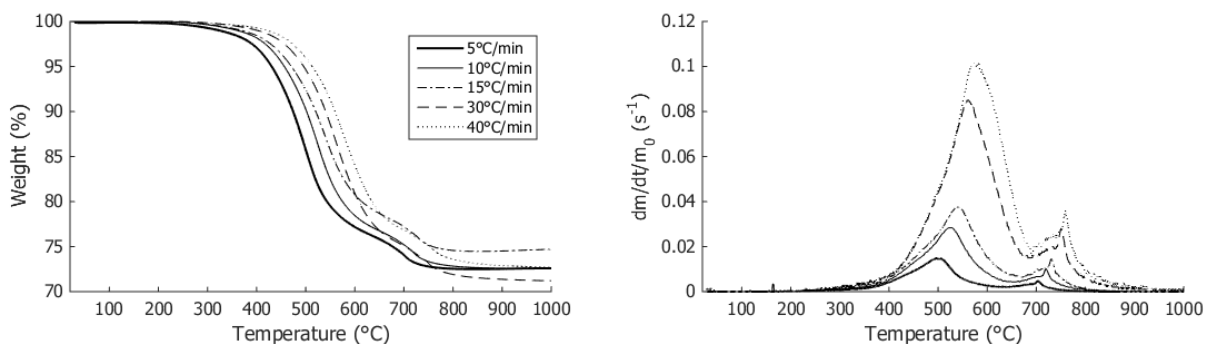


Fig. 6 Mass loss curves and derivative of the weight under inert atmosphere

Under inert atmosphere, the mass loss curves show that the degradation of the silicone-based composite begins after 400°C and concludes at 850°C for the different heating rates of the test, finally at the end of the pyrolysis, the weight lost is between 25.8% and 28.8%. Moreover, the increase in the heating rate delays the appearance of reactions, reflected by the shift of the curves to the right. To emphasize the presence of different reactions, the derivative of the weight is then studied.

The derivative of the weight loss highlights the presence of several reactions, each one associated with a peak, and confirms that at least two reactions occurs during the degradation process. One can see that degradation of the silicone-based material is characterized a first peak between 480-600°C, followed by a second between 680-780°C according to the heating rate. The delay in the appearance of reactions depending on the heating rate is thus visible in this figure. Furthermore, the peaks shifting toward higher values with the increase of the heating rate for the two main reactions.

These achieved experimental data confirms the complex thermal degradation associated with this material. For a correct estimation of the kinetic parameters triplet (E_a , A , n), a model-based method is therefore implemented. The study of the temperature derivative of the degree of reaction α is represented in Fig. 7 for a heating rate of 40°C/min under inert atmosphere. In this work, a kinetic mechanism formed by two apparent reactions is proposed to model the thermal degradation of the material under inert atmosphere. The kinetic parameters triplet is then estimated by a least mean

squares method in order to find the best fit between experimental and numerical weight loss curve. In Table 3, the results of the kinetic triplet estimations under inert atmosphere according to the heating rates are reported.

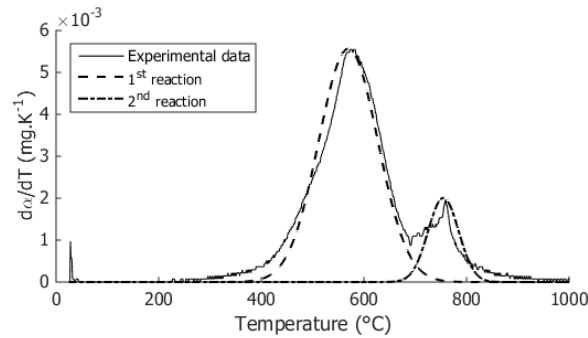


Fig. 7 Temperature derivative of the degree of reaction (40°C/min under inert atmosphere)

Table 3 Kinetic triplet estimation under inert atmosphere

	β (°C/min)	5	10	15	30	40
1st reaction	E_a (J.mol ⁻¹)	1.04x10 ⁵	1.09x10 ⁵	1.06x10 ⁵	1.14x10 ⁵	1.16x10 ⁵
	A (min ⁻¹)	9.51x10 ⁵	2.60x10 ⁶	1.64x10 ⁶	6.28x10 ⁶	8.66x10 ⁶
	n	1.38	1.38	1.37	1.35	1.34
2nd reaction	E_a (J.mol ⁻¹)	1.44x10 ⁵	1.43x10 ⁵	1.41x10 ⁵	1.40x10 ⁵	1.39x10 ⁵
	A (min ⁻¹)	8.90x10 ⁵	1.01x10 ⁶	8.91x10 ⁵	9.51x10 ⁵	1.01x10 ⁶
	n	0.98	0.83	0.72	0.70	0.59

The DSC measurement from the conventional three-step technique is reported in Fig. 8, in this study the specific heat is evaluated with a global uncertainty of 7%. The experimental data are then fitted for a better implementation in numerical model. One can see that the specific heat reaches a maximum value of 1732 J.kg⁻¹.K⁻¹ at 786°C. By comparing with the TGA curves, the maximum of the specific heat occurs at the end of the pyrolysis the material for a heating rate of 20°C/min (see Fig. 6).

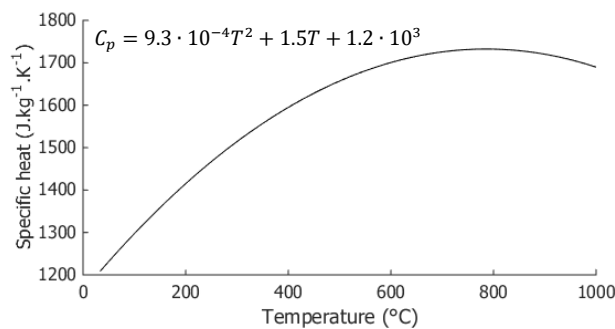


Fig. 8 Result of specific heat from DSC measurement

The dilatometry data are used to calculate the variation of the density depending on the temperature by means of the Eq. (7). The results are reported in the Fig. 9 with a global a global uncertainty of 5%. The beginning of pyrolysis at 400°C is characterized by a significant decrease in the density of the sample until the end of the test, reaching a total density loss of 25%. During the pyrolysis process of the silicon-based composite, the degradation of the polymer matrix results in the production of volatile compounds and residues of solid silica compounds, such as SiO₂ and SiCO [25-27].

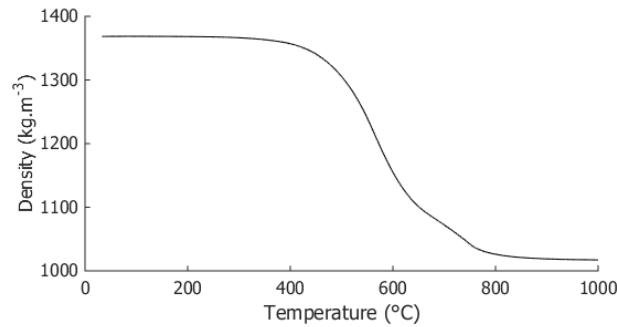


Fig. 9 Result of thermal expansion from the dilatometry measurement

From the flash method, the thermal diffusivity is evaluated before and after the thermochemical decomposition on four samples and the results are reported in the Fig. 10. The latter is fitted with a polynomial curve in order to be easily implemented in numerical model. One can observe that the thermal diffusivity of the material decreases between ambient temperature and 300°C, and finally reach a minimum value of $2.1 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$. After that, the value of the thermal diffusivity increases until the end of the experiment and reach a value of $5.1 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ at 1000°C.

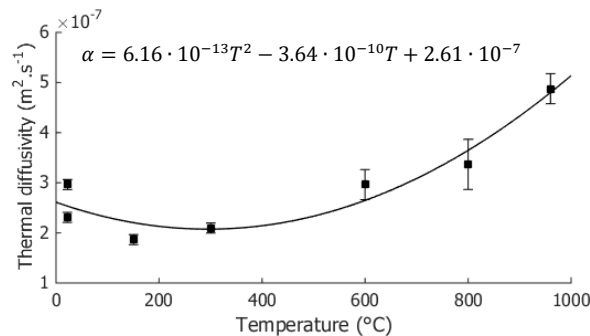


Fig. 10 Result of thermal diffusivity from the flash method

Finally, from the previous results (specific heat, density and thermal diffusivity), the thermal conductivity is calculated by means of the Eq. (8) and reported in the Fig. 11. The silicone-based composite presents a thermal conductivity of $0.41 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at ambient temperature, then the value increase to reach $0.51 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 565°C. Finally the thermal conductivity is characterized by a significant increase of the value between 600°C and the end of the experiment, to finally reach $0.84 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$.

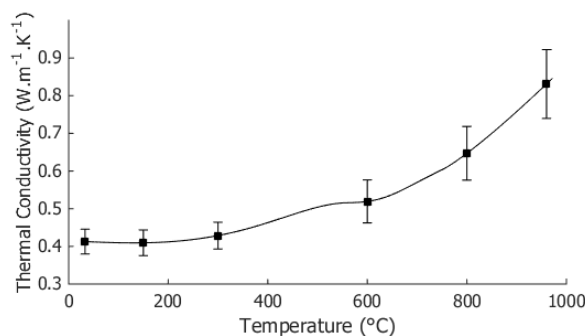


Fig. 11 Calculated thermal conductivity in function of the temperature

4.2. Numerical result

As mentioned in section 3, the measured properties are finally implemented in the numerical model to study the thermal response of the generic silicone-based material. The temperature profiles as function of time at the several positions from the heated surface (1, 2, 4, 8, 16 and 50 mm) are compared to those of TACOT "material". The comparison between the generic silicone-based and TACOT materials is sketched in Fig. 12. The material properties of TACOT and the generic silicone-based composite is proposed in the Table 4. The temperatures profiles are depicted in solid lines and dashed lines for

silicone-based composite and TACOT material respectively. From the qualitative point of view, one observes that the temperatures at several positions have the same trends for both materials. The transient temperature behaviour can be divided to two parts: transient behaviour and stationary behaviour. During the heating of samples, the transient part depends on the position where the temperature is computed. At the beginning of the heating process, the temperature gradient is almost zero at $x=1\text{mm}$. Furthermore, by observing the temperature computed at $x=8\text{ mm}$ and $x=16\text{ mm}$, a lag in the transient behaviour is noted. This lag is more important at $x=16\text{ mm}$. This is due to the heat flux resistance excreted by the materials which have relatively the same thermal conductivity. This is important as the silicone-based material constitutes a thermal barrier leading to an efficient heat flux absorption. Concerning the stationary part of the temperature behaviour, it is relatively reached only at the front face of the samples. This is due to the transient behaviour at the different locations and the relatively short test of 60 s. The temperature gradient is almost zero only at the surface, especially for silicone-based composite. By comparing the temperature evolution at the surface of both samples, it can be said that the generic silicone-based composite represents a better thermal barrier unlike to the TACOT material. From the quantitative point of view, one notes a discrepancy between the compared materials. From the surface to the back side of both materials and consequently to thermal behaviour in the compared samples low heat amount is absorbed by TACOT material. This behaviour leads to a higher temperature for TACOT material at the back face ($x=16\text{ mm}$). Therefore, silicone-based composite is more efficient as thermal barrier.

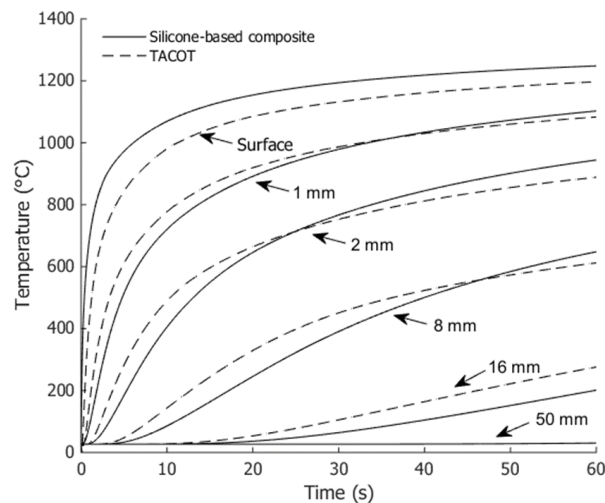


Fig. 12 Temperature profiles versus time at different locations in the silicon-based composite (solid line) and TACOT (dashed line)

Table 4 Material properties of TACOT and the generic silicone-based composite

Property	Unit	TACOT	Silicone-based composite
		Value	Value
Virgin density ρ	kg.m^3	280	1368
Char density ρ	kg.m^3	220	1027
Thermal conductivity λ	$\text{W.m}^{-1}.\text{K}^{-1}$	0.40-0.56	0.41-0.84
Specific Heat C_p	$\text{J.kg}^{-1}.\text{K}^{-1}$	879-1863	1200-1732
1st reaction			
E_a	J.mol^{-1}	7.11×10^4	1.16×10^5
A	min^{-1}	2.61×10^5	8.66×10^6
n	-	3	1.34
2nd reaction			
E_a	J.mol^{-1}	1.70×10^6	1.39×10^5
A	min^{-1}	1.08×10^{10}	1.01×10^6
n	-	3	0.59

5. Conclusion

In this work, an experimental procedure has been carried out on a silicone-based composite to determine its thermophysical properties in a large range of temperatures (up to 1000°C). Then the result of the thermophysical characteristics, such as $(\lambda, \rho, C_p, E_a, A, n)$, have been presented and implemented in a 1D numerical model to simulate its thermal behaviour. As the first part of this work, thermogravimetric analyses have been conducted, confirming the complex thermal degradation associated with this material. Under inert atmosphere, the degradation of the silicone-based composite is observed between 300°C and 800°C. Moreover, the weight of the material decreases down to 28.8%. The degradation mechanism can thus be studied by means of the derivative of the weight. One can see that the decomposition pathway of the material can be represented by at least two main reactions. From these results, a kinetic mechanism formed by two apparent reactions and a methodology are proposed for a correct estimation of the triplet kinetic parameter (E_a, A, n) . The latter is based on a model-fitting method and a least mean squares method to find the best fit between experimental and numerical weight loss curve depending on the heating rate. From this study, several apparatuses have been used to determine the thermophysical properties. Once the thermal and thermodynamic properties were determined, the measured data were implemented in the finite element 1D approach modelling the heat propagation into the material. The computations based on the measured properties within the generic silicone-based composite were confronted to that into TACOT material for different locations. The comparison has showed that the silicone-based composite represents a good thermal barrier for severe heat fluxes. Even if both materials behave similarly, the temperature at the back-face stills lower than that computed for TACOT material at the same position. The silicone-based composite is more efficient and allows, since the beginning, a good heat absorption. Because the imposed temperature at the front face does not reflect the operating conditions of real application. The present findings will further be explored at real heat fluxes on a case-study of a rocket nozzle protected thermally by silicone-based composite layer, or to a literature hypersonic reentry heat load trajectory.

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