

TG STUDIES OF A COMPOSITE SOLID ROCKET PROPELLANT BASED ON HTPB-BINDER

*J. A. F. F. Rocco*¹, *J. E. S. Lima*¹, *A. G. Frutuoso*¹, *K. Iha*¹,
*M. Ionashiro*², *J. R. Matos*³ and *M. E. V. Suárez-Iha*^{3*}

¹Instituto Tecnológico de Aeronáutica, Centro Técnico Aeroespacial, São José dos Campos, S.P., Brasil

²Instituto de Química, Universidade Estadual Paulista, Araraquara, S.P., Brasil

³Instituto de Química, Universidade de São Paulo, Caixa Postal 26077-CEP 05513-970, São Paulo, Brasil

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Abstract

Thermal decomposition kinetics of solid rocket propellants based on hydroxyl-terminated polybutadiene–HTPB binder was studied by applying the Arrhenius and Flynn–Wall–Ozawa’s methods. The thermal decomposition data of the propellant samples were analyzed by thermogravimetric analysis (TG/DTG) at different heating rates in the temperature range of 300–1200 K. TG curves showed that the thermal degradation occurred in three main stages regardless of the plasticizer (DOA) raw material, the partial HTPB/IPDI binder and the total ammonium perchlorate decompositions. The kinetic parameters E_a (activation energy) and A (pre-exponential factor) and the compensation parameter (S_p) were determined. The apparent activation energies obtained from different methods showed a very good agreement.

Keywords: AP/HTPB, Flynn–Wall–Ozawa’s method, kinetic parameters, thermogravimetric analysis

Introduction

The combustion phenomena of solid propellants are largely dependent on the propellant ingredients, pressure, propellant initial temperature, and various parameters related to the aerothermochemistry in rocket motors. In rocket motors, extreme conditions are predominant leading to temperatures of 2000–3500 K, pressures of 5–10 MPa, and estimated heating rates as high as 10^6 K s⁻¹. Combustion is an exothermic reaction involving rapid oxidizing reactions. In recent years, the theoretical and experimental aspects of chemical kinetics and the fluid dynamical nature of combustion have been understood through the use of high-speed computers and modern types of optical equipment. Because the reaction rates during combustion are much faster than those of commonly observed chemical reactions and because physical

* Author for correspondence: E-mail: maevsiha@iq.usp.br

changes, such as velocity, temperature, and pressure, accompany the combustion, aerothermochemistry is needed to understand the combustion phenomena.

Several information may be obtained from thermal studies. The thermogravimetry at low heating rates can be used to study the decomposition kinetics of solid rocket propellants formulated with ammonium perchlorate (AP) and hydroxyl terminated polybutadiene (HTPB-binder) [1–3]. Sometimes, the pyrolyzed propellant samples can be analyzed by gas-phase chromatography [4]. The thermal decomposition behaviour may be correlated to the solid propellant burning rate [5] and as it is well known the propellants based on AP exhibit a greater dependence of burning rate on oxidant particle size than propellants based on other oxidants such as cyclotetramethylene tetranitramine (HMX) and ammonium nitrate (AN). The burning rate is the prime ballistic parameter of the solid composite propellant and it can be directly correlated to the maximum decomposition reaction temperature of a determined propellant formulation.

HTPB has long been one of the most commonly used polymers in composite solid propellants. Fairly good mechanical properties are, usually, achieved when HTPB is mixed with a diisocyanate crosslinking agent, an isophorone diisocyanate – IPDI – as was used in the present study. The mixture is then cast into the desired grain configuration before it is completely cured, i.e., hardened. HTPB/IPDI serves as a ‘binder’ material to physically accommodate different propellant ingredients and it acts as a fuel constituent releasing fuel-rich gaseous products when decomposed and pyrolyzed. A plasticizer agent like DOA (di-octyl adipate) is also and frequently used to improve the casting properties.

A considerable number of decomposition and pyrolysis studies on HTPB polymers can be found in [1–5]. These studies have greatly enhanced the understanding of the detailed thermal decomposition and pyrolysis characteristics of HTPB polymers. Also, the thermal degradation of polybutadienes, including its hydroxyl and carboxyl terminated analogs, has been well studied. The uncured polybutadiene polymers show a thermal degradation in two stages. The first stage involves the carbon–carbon bond cleavages, leading to depolymerization, crosslinking and cyclization reactions. The second stage involves further degradation of the cyclized products. The thermal decomposition studies of the urethane crosslinked HTPB reveal that the urethane linkages are the first to cleave with the resultant loss of the crosslinking agent. The residual polymer decomposes as if it was an uncured binder [6].

Ammonium perchlorate, AP, is widely used as an oxidizer agent in composite solid propellants. In propellants with AP addition to the HTPB/DOA/IPDI binder the major loss steps may be primarily related to the ammonium perchlorate [7] decomposition with some degradation of the polymer binder. Also, some additives like iron oxide (Fe_2O_3) can be used in the composite formulation as a burning-rate modifier catalyst resulting in a different decomposition process which may be seen in TG-DTA curves. Thin particles of aluminum powder (15 μm) are also added to the propellant formulation (15–20 mass%) to increase the specific impulse (Isp) and it acts as a combustion instability suppressant in the solid rocket motor.

Thermogravimetric thermal analysis (TG-DTG) at different heating rates were carried out to study the thermal degradation of the 'composite' solid propellant. The TG data were applied to the Flynn–Wall–Ozawa and the Arrhenius methods to investigate the thermal decomposition kinetics.

Kinetic analysis from TG data

The kinetics of heterogeneous decomposition of solids are customarily described by the basic kinetic equation [3, 7]:

$$d\alpha/dt=k(1-\alpha)^n \quad (1)$$

where α represents the extent of reaction (degree of conversion), t is the time and, k is the rate constant. The value of α is experimentally derived from the global mass loss in TG experiments. In most cases, the temperature dependence of k can be well described by the Arrhenius equation, postulated as

$$k=A\exp(-E_a/RT) \quad (2)$$

whose substitution into Eq. (1) yields

$$d\alpha/dt=A\exp(-E_a/RT)(1-\alpha)^n \quad (3)$$

where E_a , A , R and T are the activation energy (J mol^{-1}), the pre-exponential factor (s^{-1}), the gas constant ($8.134 \text{ J mol}^{-1} \text{ K}^{-1}$) and the temperature (K), respectively.

Assuming a first order process ($n=1$), considering k from Eq. (1) and taking the natural logarithm of Eq. (2), one obtains

$$\ln k = \ln(d\alpha/dt) - \ln(1-\alpha) = \ln A - E_a/RT \quad (4)$$

Thermal decomposition of solid materials is known to involve multiple steps that are likely to have different activation energies. Then, the contributions of these steps into the overall decomposition rate measured by TG should vary with both T and α . This means that the effective activation energy determined from TG experiments will also be a function of these variables. In such situations, a commonplace approach is force the fitting to experimental data by assuming a reaction model. This approach can be used only for a TG-DTA curve using only one heating rate (β) but, it is valid only for an ideal system because in such conditions there are no changes in the reaction process as a function of the heating rate.

The Arrhenius plot of $\ln k$ vs. $1/T$ should give a straight line and the parameters E_a and A are, respectively, obtained from the slope ($-E_a/R$) and the intercept ($\ln A$).

Concerning runs at different heating rates, β , a second method can be applied to achieve the activation energy. Based on kinetics equation (Eq. (1)) for heterogeneous chemical reactions Flynn and Wall [8] and Ozawa [9–12] have proposed the so-called isoconversional method using TG/DSC curves to determine the kinetics parameters. This method is based on the isoconversional principle: the reaction rate at a constant extent of conversion is only a function of the temperature.

The Flynn, Wall and Ozawa (FWO) method is described with the following equation:

$$\log\beta = \log(AE_a/R) - \log g(\alpha) - 2.315 - 0.4567E_a/RT \quad (5)$$

where $g(\alpha)$ is a conversion functional relationship and the other terms have the usual meaning. The degree of conversion is defined as $\alpha = (m_0 - m)/(m_0 - m_f)$, where m_0 , m , m_f refer to the initial, actual and final mass of the sample. This isoconversional method allows evaluating the dependence of the activation energy on the degree of conversion without the knowledge of the explicit form of $g(\alpha)$ [13].

The activation energy determined by applying the FWO method is a sum of the activation energies of chemical reactions and physical processes in thermal degradation and therefore it is named apparent activation energy.

The use of the FWO method requires recording the $\alpha = \alpha(T)$ curves for several heating rates. For different heating rates at a constant degree of conversion, α , a linear relationship is observed between $\log\beta$ and $1/T$. Therefore, using de Doyle's approximation [14, 15], Eq. (5) was simplified and rewritten by Flynn, Wall and Ozawa as:

$$\log\beta = \text{const.} - 0.4567E_a/RT \quad (6)$$

Equation (6) was derived by assuming a constant activation energy [8] and this assumption obviously introduces some systematic error in the estimation of E_a , if it is not actually constant. However, for (E_a/RT) at $20 < E_a/RT < 60$, the Doyle's approximation leads to errors lower than 10%.

Elucidation of activation energy (E_a) is quite simple by FWO method and presents the additional advantage that any change of mechanism is obvious by changes in the slopes of the lines at different conversion degree. However, on the other hand, multiple heating rates require several samples introducing probably some errors.

Since E_a and A parameters are known, a comparison of the thermal stabilities at different heating rates (TG curves) may be done using a compensation parameter, S_p :

$$S_p = E_a / \log A \quad (7)$$

Generally, the greater value of the compensation parameter means the smaller reactivity of the system [13].

Materials and method

Initially, the ingredients except the curing agent (IPDI) are mixed thoroughly to obtain a high degree of homogeneity. Then, the desired quantity of diisocyanate (IPDI) is added and mixed thoroughly just before casting the propellant samples. The polyurethane network was obtained by curing HTPB polymer samples with IPDI at a $[\text{NCO}]/[\text{OH}]$ equivalent ratio of 0.95 at 65°C for 120 h. The NCO/OH ratio is defined as the equivalent ratio between the materials containing NCO (IPDI) groups and those containing OH groups (HTPB) and it affects the mechanical properties of cured composite propellant [9, 13]. The chemical composition of the propellant is (mass) binder 20% and others 80%.

TG/DTG curves were obtained on a model TGA 50 thermogravimetric analyser (Shimadzu) in the temperature range of 298–1200 K with heating rates 5, 15, 17.5, 30, 32.5 and 35 K min⁻¹, under dynamic nitrogen atmosphere (50 mL min⁻¹). Sample masses were about 1.8 mg and each sample was heated in Pt crucibles. The dynamic method of Ozawa was applied using the TG kinetic analysis program installed in Shimadzu Data acquisition system.

All analyzed samples were from a composite modified propellant with Fe₂O₃ and aluminum powder. The propellant samples were obtained from the same laboratorial scale batch.

Results and discussion

Figure 1 shows a typical thermogravimetric curve of composite sample obtained at a heating rate of 15 K min⁻¹. Three main steps can be observed in the thermal degradation process and this number was confirmed with the application of the onset/endset command in the Shimadzu TA 50 software. The first step around 541–573 K shows a mass loss of 6.3% and it can be related to the plasticizer (DOA) raw material degradation as pointed out by Sell *et al.* [7]. The following two steps observed in Fig. 1, respectively, are in the ranges 573–608 and 608–655 K. These steps are related to the partial HTPB/IPDI binder and total AP thermal decomposition and represent a total of 67.8% mass loss (23.9% first step and 43.9 second step).

Al-Harthy and Williams [16] applying thermogravimetric analysis by simultaneous TG/DTA curves (heating rate of 10 K min⁻¹) of AP/HTPB mixture showed that the mass loss started at 561 K and was completed at about 679 K with mass losses of 13 and 81% in the first and second stage, respectively. Therefore, the behaviour observed in the range 573–655 K, Fig. 1, is quite similar to the behaviour of the AP/HTPB mixture [16].

The last mass loss step located at 655–900 K is related to the residual HTPB/IPDI binder and corresponds to 5.4% of the initial sample mass. This result is in agreement with thermal decomposition studies [6] of the urethane crosslinked

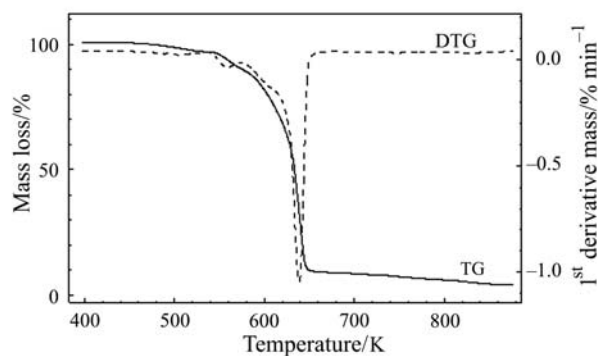


Fig. 1 TG, DTG traces for degradation of solid composite propellant (HTPB/AP) at 15 K min⁻¹ heating rate

HTPB showing that the urethane linkages are the first to cleave with the resultant loss of the crosslinking agent and the residual polymer decomposes as if it was an uncured binder. After 900 K a very small residual mass can be observed and it may be attributed to aluminum oxidation during the combustion reaction leading to the formation of alumina. The residual mass was found to be 3.7%.

Figure 2 shows the TG curves for thermal decomposition of the composite samples at the different used heating rates. The lowest heating rate, 5 K min^{-1} , led to a significant shift in the degradation temperatures to the lowest range. The beginning of the decomposition was anticipated to 525 K but three important steps were also identified and the mass losses are, respectively, 6.9, 74.2 and 15%. The last step shows a relatively high mass loss which appears, apparently, decomposed in two steps for 5 K min^{-1} , Fig. 2. This last step can also be observed for 15 K min^{-1} but with a low mass loss. These last steps disappear in the TG curves for the other heating rates.

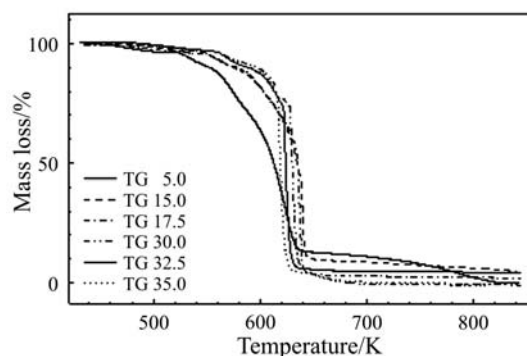


Fig. 2 TG curves of nonisothermal degradation of solid composite propellant (HTPB/AP) at 5, 15, 17.5, 30, 32.5 and 35 K min^{-1} heating rates

An increasing induction period can be observed in Fig. 2 for the first decomposition step. Three groups of experimental curves can be identified as (5 K min^{-1}), (15 and 17.5 K min^{-1}) and (30 , 32.5 and 35 K min^{-1}). According to these different induction periods, three regions can be identified in all of the curves in Fig. 2. In the range 0–25% of decomposition the onset temperatures of each decomposition step increase as the heating rate increases except for 32.5 and 35 K min^{-1} which are anticipated in respect to the 30 K min^{-1} . Between 25 and 50% of degradation the curves for 30 , 32.5 and 35 K min^{-1} show an opposite behaviour when compared to the lowest heating rates (5 , 15 and 17.5 K min^{-1}) because as the heating rate increases the decomposition temperature decreases. Above 25%, the intensity of degradation increases with the increase in the heating rates and the onset/endset ranges are very narrow. When the temperature reaches approximately 635 K, the TG curves for the highest heating rates, mainly 30 , 32.5 and 35 K min^{-1} , show different mass loss rates due to the detonation behaviour of the solid propellant samples. This detonation temperature is shifted to lower temperatures as the heating rate is increased and, the process occurs only after at least 25% of decomposition of the sample.

The FWO method was applied to all experimental TG curves obtained at different heating rates considering the degrees of conversion lower than 21% [13]. According to Fig. 2, at conversion degrees higher than 25%, an intense decomposition process can be seen and attributed to the deflagration behaviour of the samples. Figure 3 shows the plot of $\log\beta$ (heating rate) vs. $1/T$ (K^{-1}) for different degrees of conversion (α). From the slope of the curves in Fig. 3, according to Eq. (6), the average apparent activation energy was calculated resulting in (124 ± 3) kJ mol^{-1} .

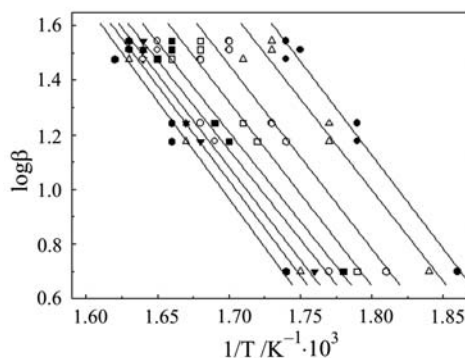


Fig. 3 Plots of the FWO method for solid composite propellant (HTPB/AP) at various fixed conversion degrees (plots from the right to the left hand-side): 0.063, 0.080, 0.096, 0.11, 0.13, 0.15, 0.16, 0.18 and 0.19

Table 1 shows the values of E_a obtained from the slopes of the curves in Fig. 3. The respective values of A (pre-exponential factor) and S_p (compensation parameter) were also calculated for each degree of conversion and they are shown in Table 1. The change of E_a is very small, isoconversional lines are parallel, which indicates the dominance of one mechanism of the reaction for the viewed thermal decomposition step (95 to 79%). The values of the compensation parameter (S_p) for solid propellant samples are practically constant, which means that the mechanism does not change,

Table 1 Kinetic parameters of nonisothermal degradation of propellant sample (HTPB/AP)

α	$E_a/\text{kJ mol}^{-1}$	$A/\text{min}^{-1} 10^{-10}$	S_p
0.063	125.0	2.045	12.12
0.080	121.6	2.145	11.77
0.096	122.7	1.567	12.04
0.112	122.7	1.179	12.18
0.128	119.4	9.069	10.90
0.145	119.4	6.995	11.01
0.161	123.9	6.202	11.48
0.177	126.7	5.741	11.78
0.194	129.7	0.5149	13.36

only the kinetics of degradation. As it can be seen in Table 1 the pre-exponential factor (A) is higher for the highest decomposition degree and almost constant for the other degrees except for the highest used conversion degree. This variation is probably not caused by a change of reaction mechanism but it is the result of experimental conditions or the physical state of the system.

Considering that the reaction mechanism could change with the increasing heating rates the isoconversional method could not be applied to the full range of the decomposition steps. But, fortunately, the FWO method could be applied to 1 by 1% decomposition steps along the TG curves considered in this study resulting in a plot of activation energy (E_a) as a function of the conversion degree (α). Figure 4 shows that E_a values are not constant over the range of the degree of conversion (α) where the isoconversional method was applied. The values of E_a corresponding to the smaller degradation percentages falls within the range 70–85 kJ mol⁻¹. The lowest activation energies are observed for $\alpha < 0.05$ and this mass loss is practically equal to the content of the DOA plasticizer propellant. However, we cannot rule out that the HTPB may also contribute to this first step. The higher conversion degrees (5–21%) considered to apply the FWO method led to higher and very closed (low standard deviation) activation energies, (124±3) kJ mol⁻¹. This apparent activation energy may be correlated to the AP decomposition and partially to the HTPB/IPDI thermal decomposition because the region ($0.05 < \alpha < 0.21$) is located in the temperature range (538–621 K) that practically coincides with the temperature of AP and HTPB/IPDI decomposition [16].

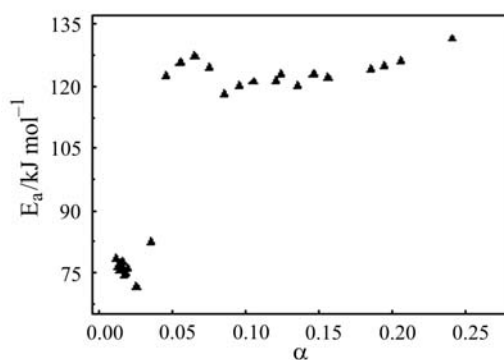


Fig. 4 Dependence of the apparent activation energy on the extent of decomposition of the propellant (HTPB/AP) samples decomposition

The kinetic parameters of thermal decomposition of propellant samples were also deduced from the TG curves using the Arrhenius method, in a very exhaustive work. The deduced activation energy varied along with the temperature ranges in each TG curve and for the different heating rates used.

The first step of decomposition exhibits an activation energy of 80 kJ mol⁻¹ for the 5 K min⁻¹ heating rate (β) and about 100 kJ mol⁻¹ for the other heating rates. The second step of degradation has a quite similar (90 kJ mol⁻¹) activation energy when $\beta = 5$ K min⁻¹ but, exhibits an abrupt change to smaller values (51±3) kJ mol⁻¹ for the

other heating rates. The activation energies for the third step defined using the onset/endset command was quite similar for all of the heating rates studied, (120 ± 15) kJ mol⁻¹, and are in a very good agreement with the value from the FWO method, (124 ± 3) kJ mol⁻¹.

Comparisons between the E_a values obtained using the Arrhenius plot and Flynn, Wall and Ozawa method must be made considering that the thermal decomposition reaction is not a first order reaction and that the decomposition steps were not the same. While the FWO method was applied to only 0–21% range of sample mass loss the Arrhenius concept could be applied up to 80% giving the E_a value for each decomposition step. On the other hand, the FWO method could be applied to a large range of heating rates recorded in this study giving an apparent E_a value that is more representative of the composite thermal decomposition along these heating rates.

For the 5 and 15 K min⁻¹ heating rates the TG curves showed the binder decomposition steps, located between 657 to 900 K. As the heating rates were increased the binder decomposition steps were shifted to lower temperatures probably because the kinetics for propellant samples thermal degradation changed. This step (binder decomposition) is strongly determined by the binder pyrolysis and AP decomposition behaviour. It can be noted that, as related by Al Harthy and Williams [16], the reactions between the binder and oxidiser products are not yet fully understood.

Conclusions

Propellants are defined as the material which generates a large number of gaseous molecules at high temperature during combustion that can self-sustain without the presence of ambient oxidizer combustion. The thermal decomposition of solid rocket propellants based in HTPB binder is a complex process that may involve various chemical and physical phenomena. Since the physical structure of composite propellants is heterogeneous, the combustion wave structure appears to be heterogeneous too. The combustion phenomena of composite propellants are largely dependent on the propellant ingredients, pressure, propellant initial temperature, and various parameters of aerothermochemistry in rocket motors [17, 18]. In a rocket motor extreme conditions are predominant leading to high temperatures, pressures and heating rates. To simulate these conditions, pyrolysis studies of solid rocket propellant and polymeric binders should be conducted at high heating rates. Thermogravimetry at low heating rates, between 35 and 5 K min⁻¹, was here used to study the decomposition kinetics of the composite propellant based on AP with HTPB binder. It was observed that the activation energy varies with the extent of composite decomposition. The slow heating rate data may happen to be irrelevant if the reaction mechanism changes with temperature. However, the difference in the temperature regions is not a sufficient condition of the change in the reaction mechanism. The reaction kinetics and mechanisms derived from the slow heating rate experiments can be used to predict decompositions under conditions of combustion [7]. Considering heating rates lower than those used in the present work (5 K min⁻¹), the results are quite similar. Sell *et al.* [7] have studied the thermal decomposition of HTPB–DOA–AP composite propellant at heating rates of 0.5,, 3.2, 3.6, 4.5, 6.8 and 9.0 K min⁻¹ and the TG

curves have also showed three major steps of the mass loss. The interrelation between E_a and α observed by Sell *et al.* [7] is quite similar to that in the present work. The first step of decomposition ($\alpha < 0.08$) exhibits an activation energy about 100 kJ mol^{-1} . The activation energy suddenly drops at the beginning of the second step ($0.08 < \alpha < 0.9$), which shows an increase in E_a from ≈ 100 to 230 kJ mol^{-1} .

Using two approaches for plotting variable heating rate data, it has been demonstrated that the Arrhenius plot may be used to obtain satisfactory values for activation energies for the decomposition of solid composite propellants. The values obtained using this approach are quite comparable to those obtained using standard variable heating rate method associated to the Flynn, Wall and Ozawa method.

The use of Fe_2O_3 as a burning rate catalyst is not denoted clearly as related by Carvalheira *et al.* [19]. Fe_2O_3 additive causes an increase in the magnitude of the exothermic DTA peaks and a decrease in the magnitude of the endothermic DTA peaks to the decreasing heating rates considering only the HTPB/IPDI polymer mixture [19]. The thermal decomposition of AP/HTPB without addition of Fe_2O_3 was studied by DSC in non-isothermal conditions, at different heating rates [20]. The Arrhenius parameters were estimated according to the Flynn–Wall–Ozawa method and the calculated activation energy was $134.5 \text{ kJ mol}^{-1}$, which is in an excellent agreement with the values found in the present work for the HTPB/AP/ Fe_2O_3 propellant, and the pre-exponential factor, A , equal to $2.04 \cdot 10^{10} \text{ min}^{-1}$ is also quite similar to those obtained in the $0 < \alpha < 0.12$ region present results.

The thermal decomposition behaviour of the solid composite propellant is affected by the heating rates used in the experiments. The reduction of heating from 35 to 5 K min^{-1} showed a shift of the decomposition peaks along different temperatures. The TG curves (different heating rate) are typical of the raw material used in solid propellant formulation and the decomposition events observed have an intrinsic correlation with the ingredients used in such formulation.

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References

- 1 J. K. Chen and T. B. Brill, *Combust. Flame*, 87 (1991) 217.
- 2 T. B. Brill and B. T. Budenz, *Progress in Astronautics and Aeronautics*, AIAA, 185 (2000) 3.
- 3 C. A. Wight, T. Sell; P. Lofy and E. Lindholm, JANNAF 35th Combustion Subcommittee and 17th Propulsion System Hazards Subcommittee Meeting: Joint Sessions, 1998, p. 129.
- 4 S. Klotz, S. T. Thynell, I. T. Huang and K. K. Kuo, *J. Prop. Power*, 8 (1992) 537.
- 5 W. Zhang and R. Zhang, *Proc. of the 22nd International Annual Conference of ICT*, Karlsruhe, Germany, July 2–5, 1991, p. 62-1 to 62-6.
- 6 L. Yeu-Cherng and K. K. Kuo, *Thermochim. Acta*, 275 (1996) 181.
- 7 T. Sell, S. Vyazovkin and C. A. Wight, *Combust. Flame*, 119 (1999) 174.

- 8 Z. Lu, Y. Ding, Y. Xu, S. Chen and Y. Yu, *J. Therm. Anal. Cal.*, 73 (2003) 333.
- 9 T. Ozawa, *J. Thermal Anal.*, 2 (1970) 301.
- 10 L. Núñez, M. Villaneuva, B. Rial, M. R. Núñez and L. Fraga, *J. Therm. Anal. Cal.*, 70 (2002) 74.
- 11 P. Budrugaec, J. M. Criado, F. J. Gotor, C. Popescu and E. Segal, *J. Therm. Anal. Cal.*, 63 (2001) 777.
- 12 Z. Liu, Y. Ding, Y. Xu, Z. Yau, Q. Liu and J. Lang, *J. Therm. Anal. Cal.*, 70 (2002) 985.
- 13 J. M. Salla, J. M. Morancho, A. Cadenato and X. Ramis, *J. Therm. Anal. Cal.*, 72 (2003) 719.
- 14 C. D. Doyle, *J. App. Polym. Sci.*, 5 (1961) 285.
- 15 C. D. Doyle, *Quantitative Calculations In Thermogravimetric Analysis*, Chapt. 4, in: P. E. Slade and L. T. Jenkis (Eds), *Techniques and Methods of Polymer Evaluation*, Marcel Dekker, New York 1996, p. 113.
- 16 A. Al-Harthy and A. Williams, *Fuel*, 77 (1998) 1451.
- 17 M. W. Beckstead, *Progress in Astronautics and Aeronautics*, AIAA, 185 (2000) 267.
- 18 S. R. Hickman and M. Q. Brewster, *J. Prop. Power*, 16 (2000) 5.
- 19 P. Carvalheira, G. M. H. J. L. Gadiot and W. P. C. de Klerk, *Thermochim. Acta*, 269–270 (1995) 273.
- 20 J. A. F. F. Rocco, J. E. S. Lima, A. G. Frutuoso, K. Iha, M. Ionashiro, J. R. Matos and M. E. V. Suárez-Iha, *J. Therm. Anal. Cal.*, 75 (2004) 551.