

THERMAL DEGRADATION OF A COMPOSITE SOLID PROPELLANT EXAMINED BY DSC

Kinetic study

*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

¹Departamento de Química, Instituto Tecnológico de Aeronáutica, CTA - São José dos Campos, CEP 12228-901 - S.P., Brazil

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

³Instituto de Química, Universidade de São Paulo, São Paulo - S.P., Brazil

Abstract

The thermal decomposition of ammonium perchlorate (AP)/hydroxyl-terminated-polybutadiene (HTPB), the AP/HTPB solid propellant, was studied at different heating rates in dynamic nitrogen atmosphere. The exothermic reaction kinetics was studied by differential scanning calorimetry (DSC) in non-isothermal conditions. The Arrhenius parameters were estimated according to the Ozawa method. The calculated activation energy was 134.5 kJ mol⁻¹, the pre-exponential factor, *A*, was 2.04·10¹⁰ min⁻¹ and the reaction order for the global composite decomposition was estimated in 0.7 by the kinetic Shimadzu software based on the Ozawa method. The Kissinger method for obtaining the activation energy value was also used for comparison. These results are discussed here.

Keywords: AP/HTPB, differential scanning calorimetry, kinetic parameters, Ozawa method

Introduction

Thermal analysis is a frequently used tool in propellants' researches [1–3]. Despite the widespread use and long investigation history of ammonium perchlorate (AP)-fuel mixtures, it still can be said that AP alone and AP/HTPB (hydroxyl-terminated-polybutadiene) composites remain among the most confounding materials in research [4]. Since the physical structure of composite propellants like the AP/HTPB composite is heterogeneous, the combustion wave structure appears to be also heterogeneous. During combustion, at the burning surface, the decomposed gases from the AP particles and fuel binder (HTPB) are interdiffused and produce diffusion flame streams. Due to this, the flame structure of AP composite propellants is complex and locally three-dimensional in shape.

The AP/HTPB composite decomposition and the combustion mechanism were extensively investigated in the last decades and the appearance of advanced methods

* Author for correspondence: E-mail: koshun@ief.ita.cta.br

of diagnostics, like flash pyrolysis, thermogravimetry and differential scanning calorimetry (DSC), led to the resurgence of the interest. These methods are widely used for the investigation of thermal decomposition of organic materials [5], polymers [6, 7], composites [8] and explosives [9].

Kissinger [10], Ozawa [11] and Flynn [12] demonstrated that DSC technique, based on the linear relation between peak temperature and heating rate, can be used to determine the kinetics parameters of a thermal decomposition (activation energy, rate constant). The Ozawa method is one of the most popular methods for estimating activation energies by linear heating rate and it is the so-called isoconversional method. Thermal analysis cannot be used to elucidate the complete mechanism of a thermal degradation but the dynamic analysis has been frequently used to study the overall thermal degradation kinetics of polymers and composites because it gives reliable information on the frequency factor (A), the activation energy (E) and the overall reaction order [13].

In the present work, the DSC technique and the Ozawa dynamic method were used to determine the kinetic parameters of the solid propellant, AP/HTPB, thermal decomposition. The Kissinger method for obtaining the activation energy value was also employed for comparison.

Experimental

Materials and apparatus

The polyurethane network was obtained by curing HTPB polymer samples with IPDI (isophore diisocyanate) at a [NCO]/[OH] equivalent ratio of 0.95, at 338 K 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 [8, 9]. The chemical composition of the propellant was (mass) binder 22% and others 78%.

DSC curves were obtained on a model DSC50 Shimadzu in the temperature range of 298–773 K, under dynamic nitrogen atmosphere (ca. 50 mL min⁻¹). Sample masses were about 1.5 mg, and each sample was heated in hermetically sealed aluminum pans. Seven different heating rates were used: 10, 15, 20, 30, 35, 40 and 45 K min⁻¹. DSC system was calibrated with indium ($m.p.=429.6$ K; $\Delta H_{\text{fus}}=28.54$ J g⁻¹) and zinc ($m.p.=692.6$ K).

Kinetic approach

The method used in the analysis of composite samples was based on DSC experiments in which the temperatures of the extrapolated onset of the thermal decomposition process and the temperatures of maximum heat flow were determined from the resulting measured curves for exothermic reactions. DSC curves (five representative curves from seven experimental curves) at different heating rates, β , for composite samples are shown in Fig. 1.

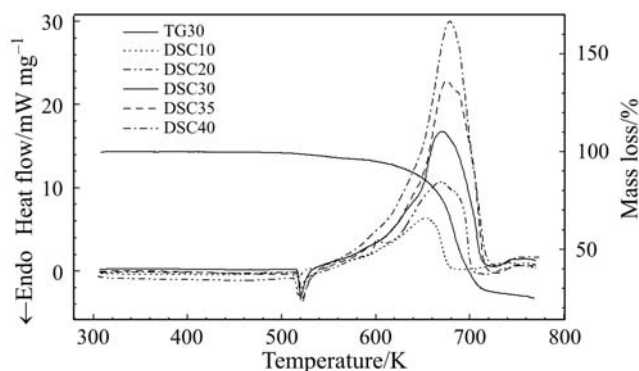


Fig. 1 DSC curves of thermal decomposition of composite samples, AP/HTPB, at the heating rates: 10, 20, 30, 35 and 40 K min⁻¹ and TG curve with a heating rate of 30 K min⁻¹

In order to determine the kinetic parameters of the degradation step Ozawa and Kissinger's methods were applied. They were both derived from the basic kinetic equations for heterogeneous chemical reactions and therefore have a wide application, as it is not necessary to know the reaction order [11] or the conversional function to determine the kinetic parameters. The activation energy determined by applying these methods is the sum of activation energies of chemical reactions and physical processes in thermal decomposition and therefore it is called apparent.

The temperatures of exothermic peaks, T_p , can be used to calculate the kinetic parameters by the Ozawa method [11, 12]. These parameters are the activation energy, E , and the pre-exponential factor, A , relative to the decomposition process.

A linear relationship between the heating rate ($\log\beta$) and the reciprocal of the absolute temperature, T_p^{-1} , may be found and the following linear equation can be established:

$$\log\beta = aT_p^{-1} + b \quad (1)$$

where a and b are the parameters of the linear equation: a is $-0.4567 E/R$ (slope) and b is a constant (linear coefficient). R is the gas constant.

Assuming that the rate constant follows the Arrhenius law and that the exothermic reaction can be considered as a single step process, the conversion at the maximum conversion rate is invariant with the heating rate when this is linear. Having such assumptions in account, Eq. (1) may be applied to the exothermic peak maximum temperature considering different heating rates [11, 14]. Thus carrying out several experiments at different heating rates a plot of $\log\beta$ vs. $1/T_p$ may be done and the activation energy can be estimated directly from the slope of the curve using the following equation derived [15] from Eq. (1):

$$E = -2.19R(d\log\beta/dT_p^{-1}) \quad (2)$$

where $-d\log\beta/dT_p^{-1}$ = parameter a (Eq. (1)).

With the above assumptions, the Kissinger method [10] may be used to calculate the activation energy and the pre-exponential factor from the maximum rate condition which will occur at the maximum exothermic peak temperature, T_p .

The Kissinger method is based on the plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$. Activation energy is calculated from the slope of the curve using the following equation:

$$E = R d(\ln \beta / T_p^2) / [d(1/T_p)] \quad (3)$$

Once E is known, the values of pre-exponential factor, A , are calculated with the equation:

$$A = (\beta E \exp E / RT_p) / RT_p^2 \quad (4)$$

The temperature dependence of the specific rate constant k is described by the Arrhenius equation:

$$k = A \exp(-E/RT_p) \quad (5)$$

The kinetic Shimadzu software, based on the Ozawa method, fed with the exothermic peak temperatures and the heating rate data, gives the Arrhenius kinetic parameters (E , A) relative to the thermal decomposition of composite and, consequently, with Eq. (5) the overall rate constant can be calculated.

Results and discussion

The activation energy and kinetic parameters of thermal decomposition of propellant samples were calculated by Ozawa method using DSC curves at seven different heating rates, 10, 15, 20, 30, 35, 40 and 45 K min⁻¹.

Five representative DSC curves are presented in Fig. 1. The DSC curves show that the first stage is endothermic and the second stage is exothermic. The endothermic event is quite similar for the different heating rates used and for all of them the peak temperature is the same. This event occurs around 520 K and it was not considered because it represents a phase transition of AP from the orthorhombic to the cubic form [15, 16]. Together with DSC curves obtained for different heating rates, Fig. 1, the TG curve for 30 K min⁻¹ was included to show that in the region corresponding to the endothermic peak (DSC curves) there is not any mass loss or, at least, it is imperceptible and, the same behavior was observed in all of other TG curves for different heating rates.

The exothermic events, Fig. 1, have different maximum temperatures (652.9, 665.9, 668.8, 683.3, 685.5, 690.1 and 695.4 K) relative, respectively, to 10, 15, 20, 30, 35, 40 and 45 K min⁻¹ heating rates.

Figure 2 shows the plot of $\log \beta$ vs. the reciprocal of the absolute temperature relative to each maximum of the exothermic stage. The value of 134.5 kJ mol⁻¹ for the activation energy is in accordance with literature despite the fact that the methods are not the same. Sell *et al.* [17] using thermogravimetry at heating rates between 0.5 and 10 K min⁻¹ studied the decomposition kinetics of the AP/HTPB propellant sam-

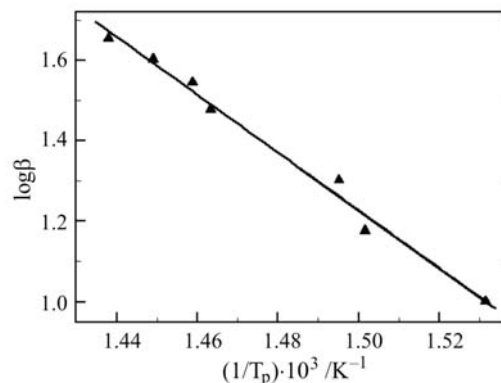


Fig. 2 Ozawa plot for AP/HTPB samples at 10, 15, 20, 30, 35, 40 and 45 K min⁻¹

ples with isoconversional method and the calculated activation energies are between 100 and 230 kJ mol⁻¹.

From the slope of Kissinger plot ($\ln(\beta/T_p^2)$ vs. $1/T_p$) and Eq. (3) the activation energy was also calculated and is 126.2 kJ mol⁻¹, therefore quite similar to that obtained using the Ozawa method.

The thermal decomposition of solid composite propellant is a multistep process and the reaction mechanism changes with the temperature and, consequently, the activation energy varies with the extent of the reaction (thermal decomposition). DSC data are used to estimate the activation energies of thermal decomposition of propellant samples because the global decomposition reaction is taken in account. The asymmetry of the peaks in the DSC curves in Fig. 1 indicates that the decomposition of propellant samples is not a single-step process. Implicit in any discussion about the decomposition is the fact that the overall process is complex, and no derived rate parameters correspond to an elementary single step. TG/DTG results are in agreement with this assumption.

The pre-exponential factor was found to be $2.04 \cdot 10^{10}$ min⁻¹ and the reaction order for the global composite decomposition was estimated in 0.7 by the kinetic Shimadzu software based on the Ozawa method. This value is quite different from the Arrhenius assumption where the reaction order is always considered 1.0. For practical purposes the Arrhenius parameters, like the corrected reaction order, can be used to estimate the overall rate constant (k) for thermal decomposition using Eq. (5). The k values for the exothermic events are very closed and the average value was calculated as $(2.95 \pm 0.02) \cdot 10^{-3}$ s⁻¹.

Cohen *et al.* [18] studied the kinetics of the surface pyrolysis of HTPB and, assuming zero-order kinetics, they found the activation energy of 71 kJ mol⁻¹. Comparison between the activation energies for the propellant decomposition and the activation energies for decomposition of individual AP or/and HTPB binder suggests that the overall kinetics of the mass loss is determined by the reaction between the binder and the decomposition products of AP [18].

AP is widely used as an oxidizer in energetic composites and it is one of the most important raw materials in propellant formulations where it represents at least 80% of

total mass of composite solid propellants, so its contribution to the thermal decomposition behavior of propellant samples is always very important. The addition of burning rates catalysts like Fe_2O_3 on the propellant formulation alters the thermal decomposition behavior of AP, and consequently the thermal decomposition behavior of the propellant. Shin-Ming *et al.* [16] showed that the presence of these catalysts compounds reduce the maximum decomposition reaction temperature in AP samples.

Another important aspect of DSC curves, as appear in Fig. 1, is the correlation of maximum temperature of exothermic peak obtained for each heating rate applied to the composite sample during the experiments. This correlation can be used to determine the burning rate characteristics of a composite solid propellant with a specific formulation. The burning rate characteristics is an important ballistic parameter of the energetic composite like solid propellant. Xiao-Bin *et al.* [19] showed that the burning rates of propellants were very closely related to the exothermic peak temperature of ammonium nitrate (AN) that is used as an oxidizer in smokeless propellant formulation.

In the present work, DSC curves at different heating rates were obtained for samples that have the same raw materials and with the same manufacture process. These conditions are necessary because differences in the raw materials, as AP particle size, can affect the thermal decomposition behavior of the composite. In other words, the decomposition mechanism of AP powder of fine particle size differs from that of AP of larger particle size.

Conclusions

For energetic materials like composite solid propellant, it is critical to use the minimum sample size and low heating rates to avoid the risks of potential damage of the DSC cell resulting in DSC curves with a lot of interferences caused by the detonation behavior of composite samples. In opposition to this criterion, in this study, high heating rates were used (10 to 45 K min^{-1}), but to compensate this condition very low sample sizes were used ($\approx 1.5 \text{ mg}$). Despite these heating rates are not close to the rocket motor chamber conditions (heating rates estimated as 10^6 K s^{-1}) the lower heating rates used in this work allow to get a better insight into the reaction kinetics mechanisms.

The Ozawa and Kissinger methods demonstrated that DSC technique, based on the linear relation between peak temperature and heating rate, can be used to determine the kinetics parameters of thermal decomposition reaction of energetic materials giving reproducible results.

The DSC curves (Fig. 1) do not show any interference and the kinetic data obtained using the maximum temperatures (reciprocal, in K^{-1}) and the respective heating rates are very close to the results found in literature, at much lower heating rates [20].

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