THERMAL BEHAVIOR OF ENERGETIC MATERIALS USED IN SOLID ROCKET PROPELLANTS

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ABSTRACT

Copolymer of 3,3´-bis(azidomethyl) oxetane and 3-azidomethyl-3-methyloxetane (BAMO-AMMO) pure and as a binder of ammonium perchlorate based composite propellant were characterized by thermogravimetric (TG) and calorimetric (DSC) analyses and compared with the thermal properties of the same composite propellant containing hydroxyl-terminated polybutadiene (HTPB) as a binder. BAMO-AMMO propellant was prepared using equal quantities of components used in HTPB propellant. BAMO-AMMO copolymer and HTPB propellant TG curves showed two and three main steps of weight loss, respectively, while BAMO-AMMO propellant presented multiples steps of weight loss. The activation energy of decomposition was estimated by isoconversional method using different heating rates in thermogravimetric experiments. BAMO-AMMO copolymer and its propellant showed different profiles of activation energy, as it was expected from the loss weight curves and considering the amount of ammonium perchlorate, which is major component (~70wt%) in BAMO-AMMO propellant. A similar range of activation energy was observed for HTPB propellant and BAMO-AMMO propellant, which increased from 100 kJ/mol to 135 kJ/mol throughout the decomposition process, while BAMO-AMMO copolymer presented activation energy changing from 160 kJ/mol to 260 kJ/mol. The energy released during the decomposition of the energetic materials was determined by heat flow curves. The profile of heat flow curves was coincident with the weight loss process for the different materials. The values of enthalpy were similar for these three energetic materials being approximately 2500J/g.

INTRODUCTION

Polymeric materials are used as binder to adhere solid particles to each other to formulate composite propellants. The main type of polymeric materials that is commonly used in composite propellants is an inert polymer, as polybutadiene acrylonitrile (PBAN) and hydroxyl-terminated polybutadiene (HTPB)[1]. In recent years, azide polymers, as 3,3´-bis(azidomethyl) oxetane (BAMO), 3-azidomethyl-3-methyloxetane (AMMO)[2,3] and glycidyl azide GAP[4], have been investigated as composite propellant binder. The decomposition of $-N_3$ bonds within azide polymers generates a significant amount of heat without oxidation reaction by oxygen atoms. The bond breakage of $-N_3$ is an initial step of the reaction accompanied by melting and gasification process[1]. These azide polymers are thermoplastic elastomers, which allows to this material overcome some disadvantages found in propellants obtained with inert binder, as the crosslinking of the polymeric molecules by chemical curing agents, which gives some restriction for the industrial processing. Additionally, once cured binder material can not be recycled because the crosslinking reaction is irreversible. The azide polymers are copolymers with rubber-like elasticity and they do not require any curing agents. For their processing, in principle, they are heated above their melting point and the solid fillers as well as the additives are added and homogenized. For the solidification the composite is allowed to cool down below the melting point. These properties are achieved because the copolymer structure contains hard and soft blocks. The hard segment (chain polymer segment that is crystalline at room temperature) confers the thermoplastic behavior, while the soft segment (rubbery at room temperature) gives the elastomeric behavior[5].

Thermal decomposition of energetic materials has been studied by thermogravimetric and calorimetric analysis[6-9].

In the present work, a thermal decomposition comparative study was performed for BAMO-AMMO copolymer and its propellant, as well as HTPB propellant, both based in ammonium perchlorate. The activation energy was calculated from thermogravimetric experiments for all materials by isoconversional method, and the enthalpy of decomposition was estimated by calorimetric analysis.

EXPERIMENTAL

BAMO-AMMO copolymer was synthesized in accordance with literature[5]. Two composite propellants were used, one of them containing the BAMO-AMMO copolymer as a binder, and the other based in HTPB. Both propellants contained 70wt% of ammonium perchlorate and 15wt% of aluminum powder. Thermogravimetric and calorimetric experiments were carried out in a simultaneous DSC-TG, SDT Q600 TA Instruments, under nitrogen atmosphere. About 3 mg of each sample were placed in alumina covered cell. The heating rates used were 1, 2 and 3ºC/min for BAMO-AMMO copolymer and its propellant, and 2, 3 e 4ºC/min for HTPB propellant. The analyses were conduced in a temperature range from 150 to 500ºC. All analyses were done in duplicate and the values reported are the average of these two individual values. The temperature of the thermal decomposition for all materials was determined by the maximum of the peaks in derivative thermogravimetric curves (DTG).

DISCUSSION

BAMO-AMMO copolymer and its propellant showed self ignition at heating rate superior to 3ºC/min, while ignition was observed for HTPB propellant above 4ºC/min, which delimited the range of heating rate used.

TG curves obtained at different heating rates for BAMO-AMMO copolymer and its propellant, as well as for HTPB propellant and ammonium perchlorate (AP) are shown in Figure 1. In this figure (1-a, 1-b and 1-c) the DTG curve was shown only for the analysis obtained at lower heating rate in each case, and theses curves were presented in order to show clearly the weight loss steps in each material. Different heating rates were used in TG experiments for allowed the calculation of the activation energy by multiple heating rate method, which will be discussed later.

BAMO-AMMO copolymer shows two well defined steps of weight loss due to the decomposition of copolymer (Figure 1-a), while BAMO-AMMO propellant presents multiple weight loss processes (Figure 1-b). BAMO-AMMO propellant contains 70wt% of AP in its composition, and when its TG curve is compared with TG curves of AP (Figure 1-d) and BAMO-AMMO copolymer (Figure 1-a), it can be seen that BAMO-AMMO propellant shows decomposition processes which can be associated to both materials, which make more complex this propellant thermal decomposition. The temperature of the weight loss initial stage for BAMO-AMMO propellant was 222ºC, which was similar to those observed for BAMMO-AMMO copolymer (225ºC) and

lower to that observed for AP decomposition (310ºC), suggesting that the weight loss initial step in BAMO-AMMO propellant should be due to the thermal decomposition of BAMO-AMMO copolymer.

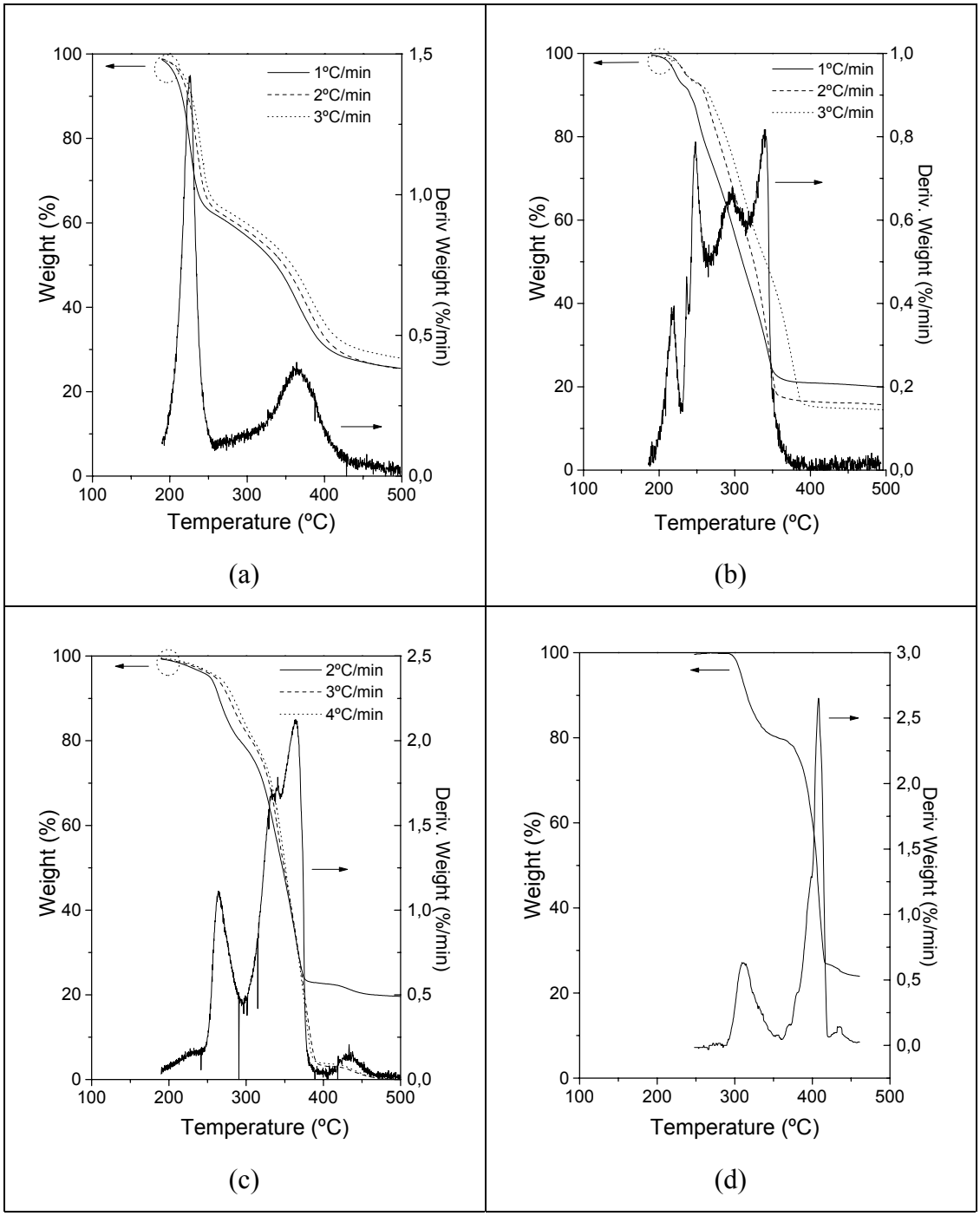


Figure 1: TG curves obtained for: (a) BAMO-AMMO copolymer, (b) BAMO-AMMO propellant, (c) HTPB propellant (d) AP at 5ºC/min. DTG curves were shown only for the run obtained at lower heating rate in (a), (b) and (c).

Oyumi et al.[9] also observed the decreasing of initial temperature of thermal decomposition in AMMO/AP propellants in relation to the initial temperature of AP thermal decomposition. This behavior was related to the AMMO presence, which dominated the decomposition process initiated by nitrogen gas evolution from the methylazide group. In the initial stage, the weight loss observed for BAMO-AMMO propellant was about 7%, which was the weight loss expected for the first step, considering that the content of BAMO-AMMO copolymer in the propellant was 15%. The addition of the others weight loss steps was about 70%, which is coincident with the AP content.

HTPB propellant TG curves at different heating rate are shown in Figure 1-c. This composite propellant also contained 70wt% of AP, meanwhile, the thermal decomposition of the polymeric matrix was overlapped by AP decomposition, which confers a similar profile of HTPB propellant TG curve to those observed for AP (Figure 1-d). In this case, the temperature of weight loss initial stage is 263ºC, higher than those observed for BAMO-AMMO propellant and lower than AP measured initial decomposition temperature (310ºC).

The first stage of weight loss in HTPB propellant occurs in the temperature range of 100-260ºC, and the propellant loses about 20%. In the second stage it can be observed a weight loss of 56% at temperature between 260 e 420ºC. In a third weight loss step about 3% is lost. At 500ºC in the end of the heating the residue remained was about 19%, which can be associated to aluminum content (~15wt%) and to the others residual materials.

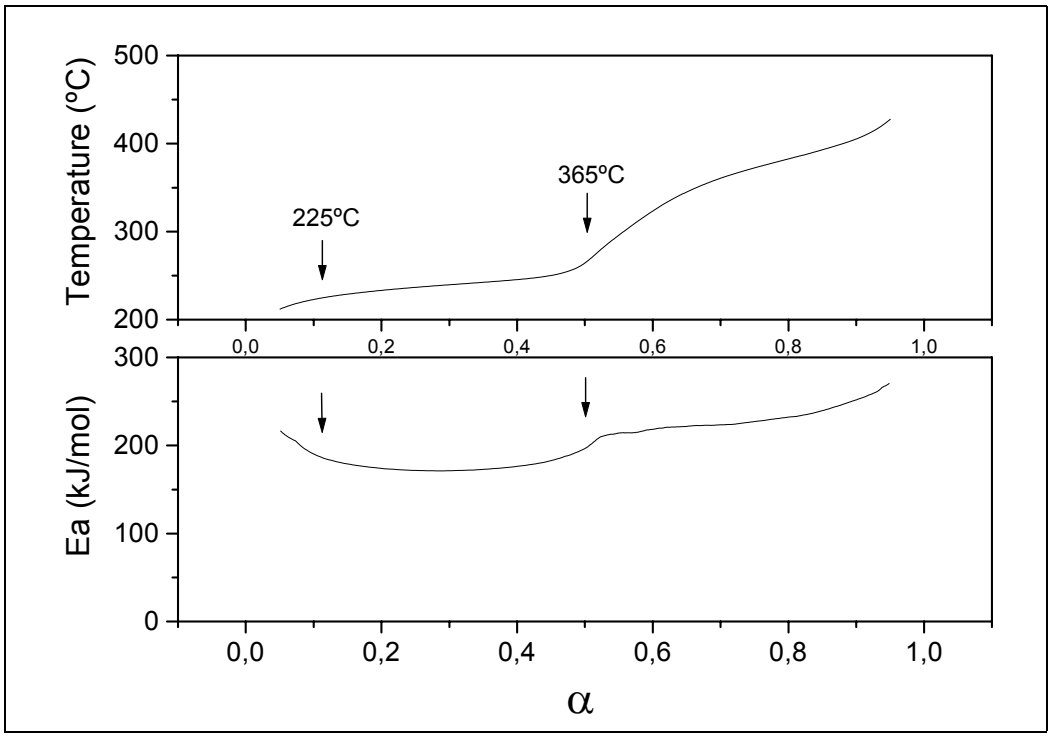
The activation energy (Ea) was calculated from the TG curves using the isoconversional method, which allows evaluated the effective activation energy as a function of the extent of conversion (α). The activation energy tends to vary with the last one[6, 10].

Curves of temperature and activation energy as a function of conversion for BAMO-AMMO copolymer and its composite propellant are shown in Figure 2.

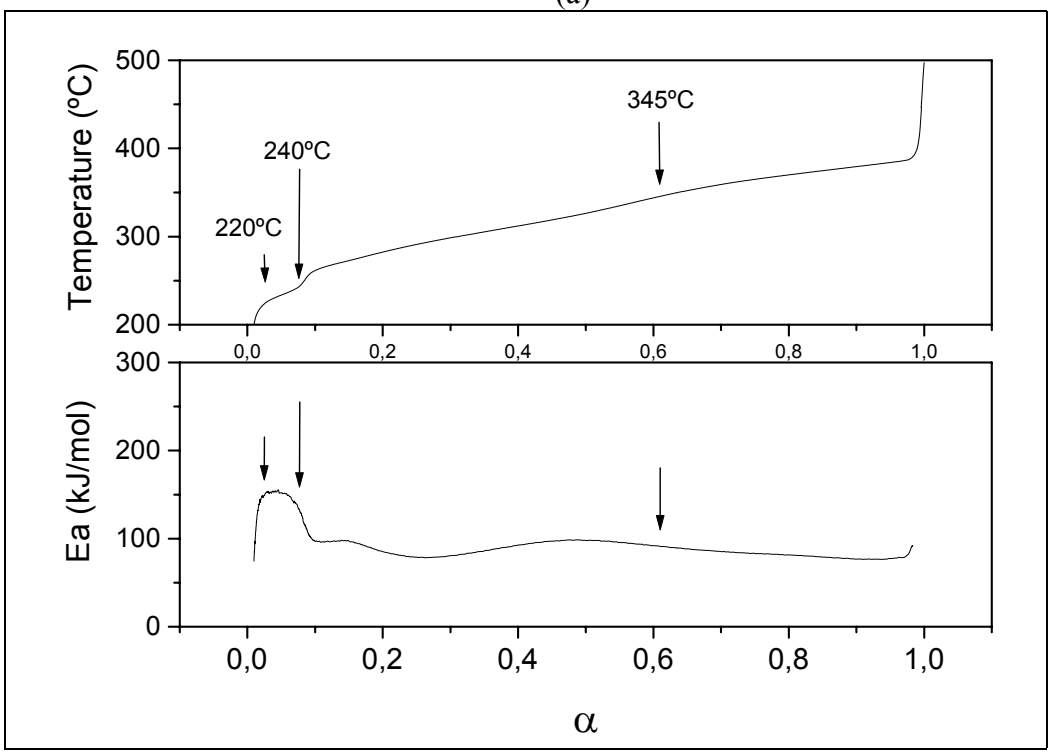
The activation energy is associated to each decomposition process present in the material, consequently, Ea changes in accordance with the weight loss due to the thermal decomposition. This behavior is indicated in Figure 2 by the arrows.

The activation energy for BAMO-AMMO copolymer (Figure 2-a) changed from 215 to 171kJ/mol (α= 0.0 to 0.3) and from α > 0.3 to the end of the thermal decomposition Ea increased to 260kJ/mol. Nair et al.[11] reported activation energy for

polyBAMO as 163kJ/mol. As AMMO is a molecule less energetic than BAMO[7], it was expected that the presence of AMMO in the copolymer increases the activation energy for the beginning of the thermal decomposition.



(a)



(b)

Figure 2: Temperature and activation energy as a function of conversion for (a) BAMO-AMMO copolymer and (b) BAMO-AMMO propellant.

The activation energy obtained in the first stage of decomposition of BAMO-AMMO propellant (Figure 2-b) changed from 75 to 97kJ/mol (α=0-0.1) with a maximum at 155kJ/mol. In the second weight loss step the activation energy showed a small variation (77-98kJ/mol). The result reported by Sell et al.[6] for activation energy obtained for a composite propellant based in BAMO-AMMO copolymer and containing about 60wt% of AP was 120±20kJ/mol (α=0.2 to 0.9). In the present work, the profile of activation energy curves was similar to those found by Sell et al.[6], however, it was observed a light displacement in the activation energy position in relation to the conversion values. The BAMO-AMMO propellants studied by Sell et al.[6] contained 11,99wt% of glycidyl azide polymer (GAP) as a plasticizer, which can be the responsible for these differences.

The average relative error of activation energy calculated for BAMO-AMMO copolymer and its propellant was 6%, varying from 1 to 17% in all the extension of α. This result is satisfactory because the relative error for three heating rates is estimated in 26%[12].

The activation energy for HTPB propellant at the first weight loss step increases up to 88kJ/mol at α=0.06 (Figure 3). Before the second weight loss stage, it can be observed a decreasing in the activation energy to 47kJ/mol at α=0.2. In the second stage, the activation energy increases to 110-135kJ/mol up to the end of the temperature range analyzed. This value is close to those found by Rajendran et al.[13] for aluminum/ammonium perchlorate mixture, which showed Ea values varying between 92,2 and 127,6kJ/mol as determined by Ozawa's method from DSC multiple heating rate. However, the activation energy obtained in the present work was lower than those reported by Sell et al.[6] for a composite propellant based in HTPB, which presented activation energy in the second step changing from 100 to 230kJ/mol. It should be considerate that HTPB used by Sell et al.[6] did not contain aluminum, which could be responsible for the difference observed.

The relative error of activation energy for HTPB varied in the same range observed for BAMO-AMMO materials (1 to 17%), and the average relative error was 4%.

Comparing the performance of BAMO-AMMO copolymer with its propellant from activation energy results, it can be seen that the addition of AP in BAMO-AMMO copolymer decreased the activation energy value, which changed from 160-260kJ/mol for the copolymer to approximately 100kJ/mol for the propellant.

The substitution of HTPB binder for BAMO-AMMO copolymer in composite propellant, caused the reduction of the initial temperature of propellant thermal decomposition althoug the activation energies were very closed in both propellants, approximately 100kJ/mol for BAMO-AMMO propellant and 110-135kJ/mol for HTPB propellant, suggesting that the activation energy behavior is mainly determined by ammonium perchlorate decomposition.

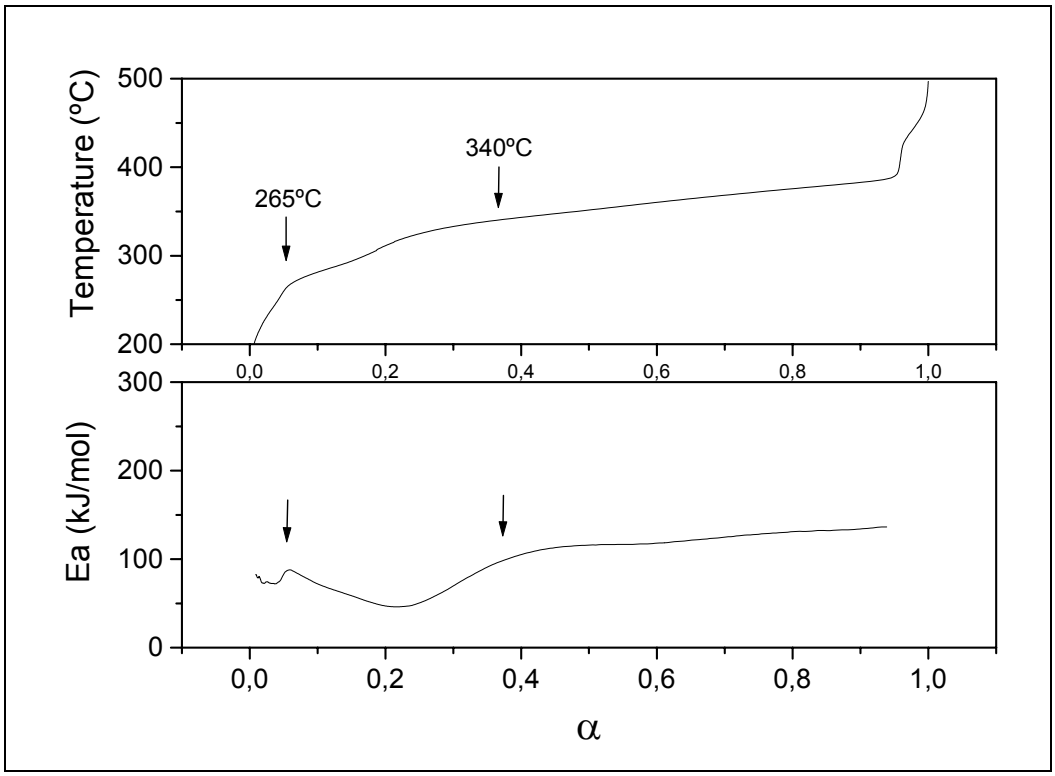


Figure 3: Temperature and activation energy curves as a function of conversion for HTPB propellant.

Heat flux curves (DSC) were obtained simultaneously to TG analysis, and the decomposition enthalpy was calculated from these curves for all studied materials (Figure 4 and Table1). The endothermic peak near 250ºC is due to the orthorhombic to cubic structure lattice phase transition[1].

The enthalpy of thermal decomposition was practically equal for both propellants studied, and lightly higher for BAMO-AMMO copolymer. The enthalpy of HTPB binder (without energetic fillers) also is presented in Table 1. Comparing the enthalpy values obtained for inert (HTPB) and energetic (BAMO-AMMO copolymer) binders it was expected that HTPB propellant presented lower enthalpy value.

Meanwhile, as it was suggested by activation energy behavior, in this case the enthalpy value should also be determined mainly by AP thermal decomposition, which is the major component in both propellant compositions studied.

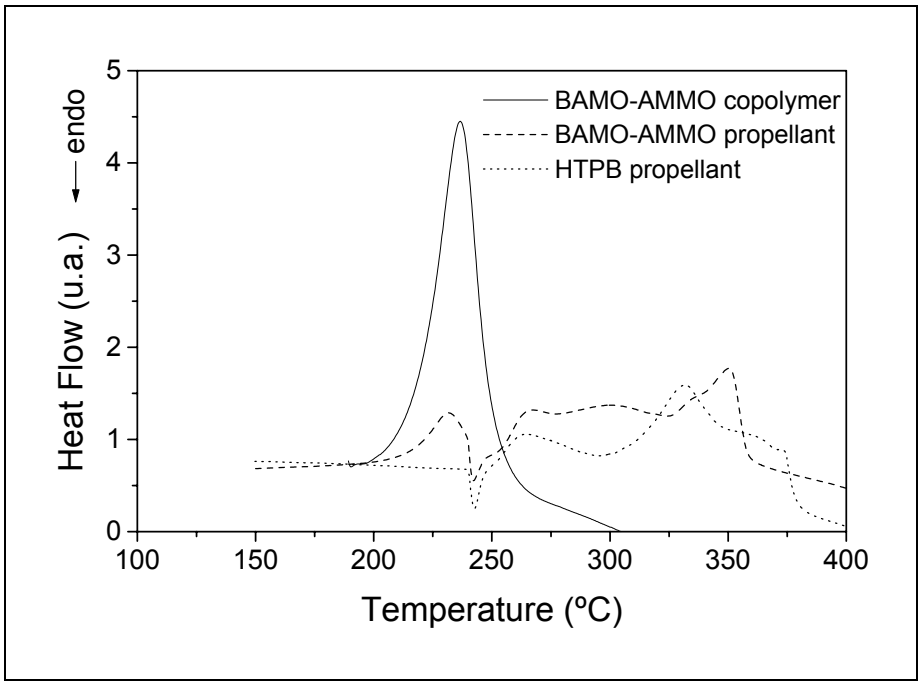


Figure 4: Curves of heat flow as function of temperature for energetic materials obtained at 2ºC/min.

Table 1: Enthalpy of decomposition for energetic materials.

Material	**ΔH (J/g)**
BAMO-AMMO copolymer	2625±180
BAMO-AMMO propellant	2294±76
HTPB propellant	2231±2
HTPB binder*	698±34

*HTPB and IPDI (isophorone diisocyanate) cured without energetic fillers (AP and aluminum)

CONCLUSION

BAMO-AMMO propellant, which contained 70wt% of ammonium perchlorate, showed a significant reduction in activation energy for the beginning of the thermal decomposition in relation to BAMO-AMMO copolymer.

In spite of the thermal decomposition of BAMO-AMMO propellant to start at lower temperature than those observed for HTPB propellant, the activation energy obtained for both propellants was similar, suggesting that in the studied composition this parameter is mainly determined by ammonium perchlorate decomposition.

The enthalpy values observed for BAMO-AMMO propellant and HTPB propellant also suggests that this parameter in the propellant composition studied was mainly determined by ammonium perchlorate thermal decomposition, as this values are similar, even though, the BAMO-AMMO copolymer presented very higher enthalpy value than HTPB unfilled.

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