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Aging Evaluation of Ammonium Perchlorate/Hydroxyl Terminated Polybutadiene-Based Solid Rocket Engine by Reactive Molecular Dynamics Simulation and Thermal Analysis

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***Abstract*—**Propellants based on Hydroxyl Terminated Polybutadiene/Ammonium Perchlorate (HTPB/AP) are the most commonly used in most of the rocket engines used by the Brazilian Armed Forces. This work aimed at the possibility of extending its useful life (currently in 10 years) by performing kinetic-chemical analyzes of its energetic material via Differential Scanning Calorimetry (DSC) and also performing computer simulation of aging process using the software Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). Thermal analysis via DSC was performed in triplicates and in three heating ratios (5 ºC, 10 ºC, and 15 ºC) of rocket motor with 11 years shelf-life, using the Arrhenius equation to obtain its activation energy, using Ozawa and Kissinger kinetic methods, allowing comparison with manufacturing period data (standard motor). In addition, the kinetic parameters of internal pressure of the combustion chamber in 08 rocket engines with 11 years of shelf-life were also acquired, for comparison purposes with the engine start-up data.

***Keywords*—**Shelf-life, thermal analysis, Ozawa method, Kissinger method, LAMMPS software, thrust.

I. Introduction

ROCKET engines are the driving and propelling force for major warlike artefacts such as missiles and rockets launched either from aircraft, vehicles and/or auxiliary devices. In view of the need for several countries, including Brazil, to maintain their readiness in the event of war, armaments are stocked and stored for a long period of time, may exceed its useful life, now established in 10 years for most rocket engines containing propellants based on HTPB/AP.

After a shelf-life, the rocket motors are discarded, since the manufacturing requirements will no longer be fulfilled, and consequently, their operation and use may be jeopardized in a safe way.

Studies are done to identify changes in rocket motor properties due to aging, which may affect the safety or performance of the artefact. A small failure in the propellant grain can change its behavior in flight or cause the loss of a missile altogether.

The chemical aging of energy materials is an important factor for the determination of their time of use, since they affect the properties of the energetic material (enthalpy, activation energy, etc.) and the mechanical properties (hardness, elongation of rupture, etc.) propellant, so that it may compromise the flight's ballistic properties of the system [1].

The useful life prediction of a composite material, for example, such as a propellant material, can be estimated through analytical chemistry analyzes, among them thermal analysis, kinetic decomposition calculations, and chemical stability analysis [2]. These techniques of thermal analysis have been widely used because of their safety, since they require only small samples, and also allow the study in isothermal and non-isothermal modes under different temperature and atmosphere conditions [2].

One of the most used techniques in the literature is the thermal analysis by DSC, a technique used for research purposes in this article, according to the ASTM E698/11 ―Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials Using DSC and the Flynn/Wall/Ozawa Method‖ [3].

This analysis was chosen because it allows the acquisition of kinetic parameters from samples of aged propellants on the shelf with 11 years of shelf-life, with relatively low costs.

The consequences of a chemical aging of the energetic materials are the changes in the kinetic/chemical properties, due to the increase of cross-links in the polymer chain [4], which may result in increased grain surface hardness, swelling, debonding of interfaces of the propellant grain near the engine tube, in addition to the appearance of internal cracks that can cause an increase of burning area [5], and consequently, a possible explosion of the warlike artefact.

Another very important factor that can cause operational failure in a combat military aviation is the change in values of its kinetic properties, such as thrust of a rocket motor and the increase of the internal pressure inside its combustion chamber, in this case, it may collapse until a catastrophic failure.

Rocket propellants are used to generate high temperature and high-pressure combustion products in a rocket motor. The main design criterion for a rocket motor is to obtain a desired

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pressure versus firing time curve in order to obtain a required thrust versus desired time curve [6].

Rocket engines loaded with solid propellant composite are the propulsive energy of major warlike artefacts produced in the market. However, the energetic material in which it is composed in its interior, deteriorates over time, due to the chemical aging of its polymer matrix formed by PBLH/AP and other complementary additives.

The rate of deterioration of the rocket motor depends on the environmental conditions of storage and stocking [7]. The evaluation of a product before entering service is carried out fulfilling the norm of qualification of energetic materials [9], [10].

One of the models used for the kinetic calculation of thermal decomposition of energetic materials as a function of temperature is the Arrhenius equation. This method is used taking into account that the whole process is constituted by first order reactions. In higher order reactions, it is necessary to take into consideration the molecularity factor of each elemental reaction, directly related to the system temperature [8].

From the Arrhenius equation, several models were developed for kinetic calculations of thermal decomposition of materials in the solid state, among them the energetic materials.

The objective of the present work was to analyze the aging of a solid propellant rocket engine, based on kinetic models applied on thermal analysis results and a reactive molecular dynamics simulation.

II. Methodology

A. DSC

The thermal analysis via DSC was carried out in a DSC-60 equipment from SHIMADZU Corporation.

The propellant grains were withdrawn from the central region, that is, from the region located between the surface of the star tip and the region near the liner of the rocket motor tube, whose samples were cut and weighed at approximately 1.0±2 mg.

The analyses were performed in triplicates for each heating rate at 05, 10, and 15 ºC/min, programmed to start from room temperature up to 450 º C. The DSC analyses were performed to obtain the peak temperature data (K) of the exothermic reaction, onset and endset temperatures, and enthalpy change (ΔH), with the objective of determining the thermal decomposition parameters of activation energy, using the Ozawa [11], [12] and Kissinger [13], [14] methods.

TABLE I
Composition of the Solid Propellant

Constituent	Concentration (m/m%)
HTPB	15
AP	70
Other components (binding agents, IPDI, curing agents etc.)	15

The solid propellant of the composite type, object of this study, was the HTPB/AP and presented the following compositions at an approximate percentage level (Table I).

B. Reactive Molecular Dynamics Simulation

The reactive molecular dynamics simulations were performed using the software LAMMPS and the ReaxFF force field. ReaxFF has a fundamental assumption where the bond order and bond energy between a pair of atoms is obtained from the interatomic distance.

ReaxFF force fields are developed/optimized using successive one-parameter search technique, in which all obtained data are from quantum chemical calculations (Density Functional Theory - DFT). Heats of formation to within 4.0 kcal/mol were reproduced using this technique.

The condensed phase structure of a solid propellant, composed by AP and HTPB, in a proportion of 0.715:0.1576, was used in the combustion simulation. The molecules were inserted in a unit cell measuring 31 x 31 x 31 Å, generating a condensed phase structure with approximate density of 1.54 g cm^{-3} (experimental density: 1.75 g cm^{-3}).

In the beginning of the simulation, an energy minimization at low temperature was done in the system. The system was then subjected to an NVT ensemble (constant number of atoms, volume and temperature) during a short period, for the molecules to acquire a steady state. For the production phase of the simulation, an NVE ensemble was used. As the current simulation involves fast reactions, a timestep of 0.1 femtoseconds (fs) was used. The total simulation time was 100 ps for the selected temperature of 328 K (temperature of the aging test). The temperatures were controlled by the Berendsen thermostat, with temperature damping constant of 100 fs.

As the aging process would require a simulation in a non-feasible timescale, the aging of the sample was simulated by shrinking linearly one of the dimensions of the cell, from 31 to 24.8 Å. This procedure was done due to the known behavior of propellants to shrink its volume as the material ages, because of the increase on the crosslink density of the HTPB.

III. Results and Discussion

A. DSC Analysis of Rocket Engine Propellant with 11 Years of Shelf-Life

DSC analyses of 11-year shelf-life propellants were carried out, in triplicates and at 03 heating rates (5 ºC, 10 ºC, and 15 ºC), as shown in Fig. 1.

TABLE II
DSC Exothermic Peak Results of Shelf-Life 11-Year Propellants

β (ºC/min)	Onset	Endset	Area (J)	ΔH (kJ/g)	Temp. Peak (K)	Tp avg (K)
5	313.06	349.22	0.1616	0.167	612.32	
5	319.57	346.10	0.1017	0.1037	609.07	610.6
5	319.86	347.23	0.0829	0.0831	610.42	
10	343.47	365.42	2.24	2.21	629.68	
10	326.34	374.01	2.35	2.35	632.49	630.9
10	340.01	366.99	2.40	2.35	630.46	
15	350.35	378.28	2.90		638.01	
15	349.38	363.34	2.55	2.52	633.01	635.1
15	348.27	374.93	2.73	2.78	634.32	

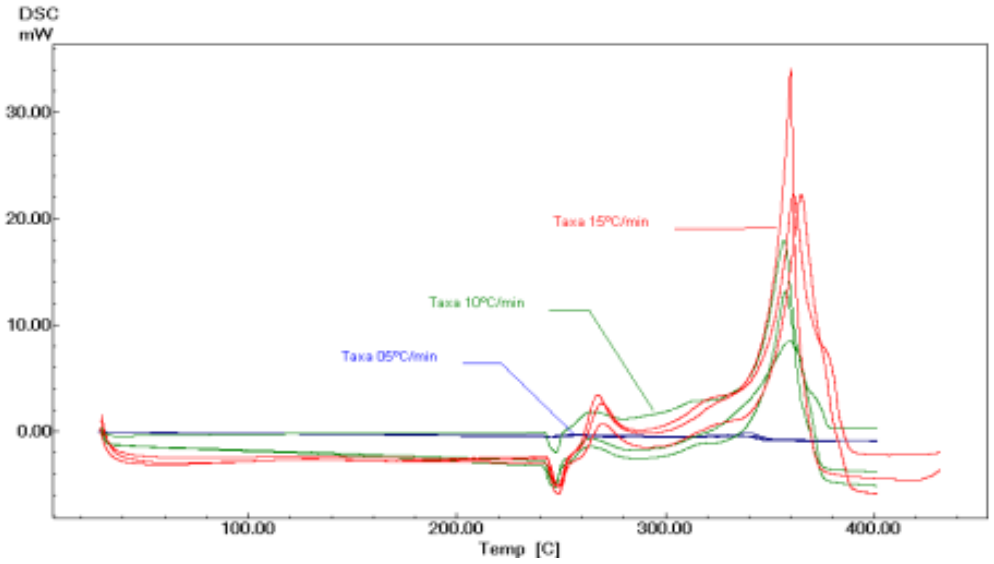

Fig. 1 DSC analysis of 11-year shelf-life propellant in triplicates and in three heating ratios

Then, the results of the exothermic peak such as, onset, endset, enthalpy change (ΔH) and peak temperatures are presented in Table II, all in triplicates and in 03 heating ratios, whose values were used to obtain the activation energy (Ea).

From the heat flow data, or DSC, presented in Table II, the linearization graph between log β versus (1/Tp) x10³ was plotted using the Ozawa method according to Fig. 2, and the graph ln (β/Tp²) versus (1/Tp) x10³ was plotted using the Kissinger method according to Fig. 3.

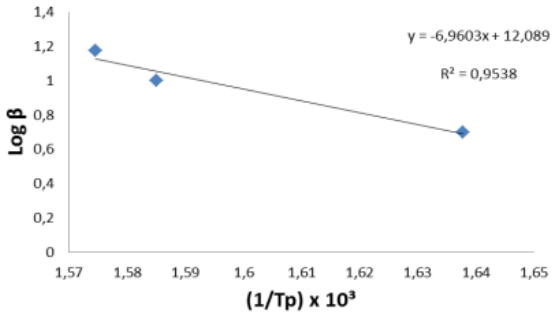

Fig. 2 Linearization curve by the Ozawa method for shelf-life 11-year propellants

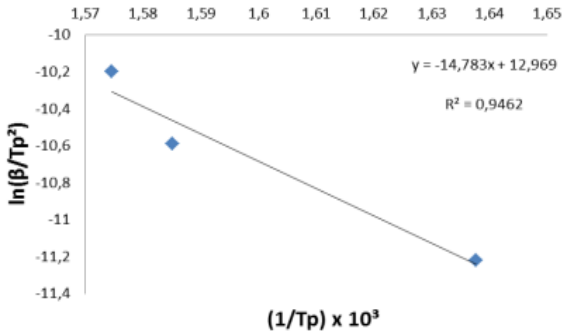

Fig. 3 Linearization curve by the Kissinger method for 11-year shelf-life propellants

In addition to the linearization of the points in the graph, results from the maximum peaks, the linear equations and their respective determination coefficients R^2 were also obtained, for the purpose of measuring data related to the adjustment of the model used.

Comparing the values of R^2 in Figs. 2 and 3, it is possible to verify that there is a greater linearity using the Ozawa method, even if insignificant, presenting the value of 95.38%, when compared with the Kissinger method, about 94.62%.

A low value of the correlation coefficient can mean in practical terms, from changes in the behavior of the sample according to its heating rate, even the fact that the mass and shape of the sample are different for each analysis [1].

Based on the straight equations presented above, the values of the activation energies (Ea) were obtained as shown in Table III.

TABLE III
ACTIVATION ENERGY RESULTS USING OZAWA AND KISSINGER METHODS

Activation energy (Ea) in kJ mol^{-1}	
11-year shelf-life propellants	
Ozawa	126.67
Kissinger	122.85

Initially, a low disparity/deviation in Ea scores between the two methods can be verified, about 3.01%. This variation is probably due to the difference between the values of the correlation coefficient previously discussed.

For the purpose of comparison of results and Ea values, there is in the literature several information and activation energy values of aged propellants based on HTPB/AP based on degradation carried out by several types of analysis such as mechanical properties and / or thermal analysis via DSC.

One of these studies carried out by SHEKHAR (2011) [15], a propellant was considered degraded with a shelf-life estimated around 20 years, whose Ea value found under these conditions was 72.8 kJ.mol^{-1}, considering a natural aging at an

average temperature of 27 ºC. This study was based on the criterion of degradation from mechanical properties of elongation as 50% its limit value.

A low value of Ea is directly related to the aging of propellant grain, that is, the energy material is degraded and more sensitive to heat. In practical terms, the propellant may be easier to ignite compared to less sensitive and/or more preserved propellant.

Another study also carried out on the basis of HTPB / AP performed by GONCALVES; ROCCO; IHA (2013) [4] presented an activation energy value for aged propellant at 79 kJ.mol^{-1}, using the Ozawa kinetic method, based on DSC thermal degradation analysis. Thus, it is possible to affirm preliminarily that the rocket motors containing HTPB/AP propellants in this study present Ea values well above those found in the literature, demonstrating that it is still possible to maintain a certain operational continuity and prolong the useful life of these energy materials.

B. Result of Computational Simulation of Aging

ReaxFF reproduced with acuity all relevant quantum mechanical data, as well as provided atomistic descriptions of several complex chemical reactions.

In Fig. 4, the result of this simulation was presented in which it was submitted to a group of molecules of composition HTPB/AP in the same proportions of the composition of propellant in study in this work. In this graph, it can be verified that the distance on the X-axis at 0 ps (peak seconds) is 31Å, whereas, at 4ps the distance of this axis decreased to 28.52Å, at 6ps the distance was 27.28 Å, and at 10ps the distance dropped to 24.8 Å, whose total reduction was about 20% compared to its initial state.

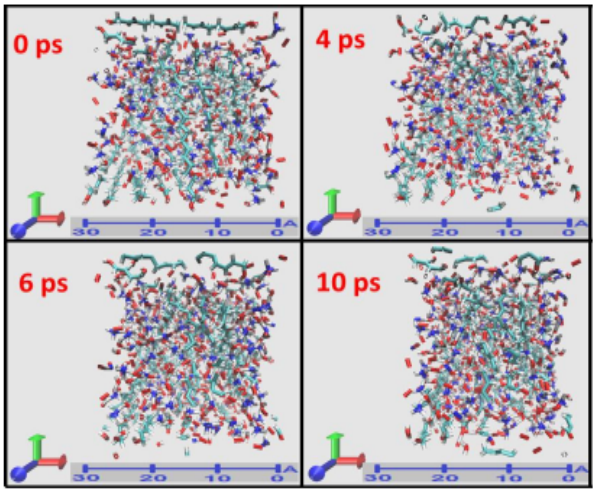

Fig. 4 Computational simulation results in 0, 4, 6, and 10 ps

At every MD (Molecular Dynamic) step, the force field through ReaxFF updated the bond orders and provided a pathway for bonds to form and break during the course of the simulation.

This breakdown of its original chemical bonds gave rise to new smaller chemical bonds, resulting in an increase in its density, exhibiting an initial change from 1.54 g/cm³ (0ps) to 1.86 g/cm³ (10 ps), and consequently, showing an increase in their crosslinks. This molecular rearrangement in the system was evidenced with the variation of its potential energy versus volume, as shown by Fig. 5, in which it can be observed that the force applied to the system stimulates the increase of its potential energy, which in turn, for the purpose of stabilizing, the breakdown of its chemical bonds occurs forming other bonds, and consequently, resulting in the decrease of its volume. This cycle was evidenced and carried out until the reduction of 20% of its initial volume in the X-axis.

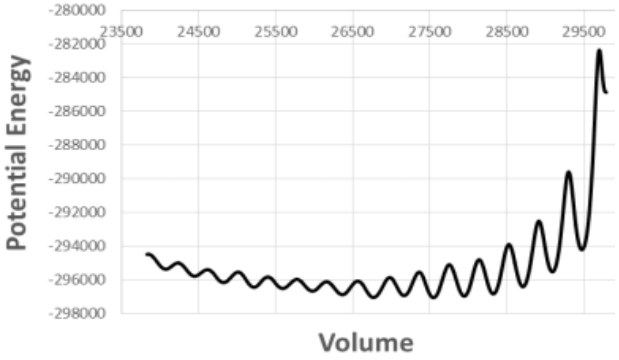

Fig. 5 Variation of potential energy versus volume from rearrangement of HTPB/AP molecules

The balance of this system occurs to the lowest point of the inflection curve of the graph, when its volume is approximately 26.500 (Å)³. From this point on, the equilibrium is no longer presented, and its potential energy is increased to force the continuity of its reduction. In practical terms, by continuing to reduce it, an increase in internal stresses may occur causing a cracking and/or internal fracture of a particular propellant. With this, the computational simulation allowed to evaluate the importance and the understanding of the mechanism of aging of a propellant, associated with the reduction of its volume and the increase of its crosslinks, and if using a rocket motor in a real mission, with its expired useful life, could cause even a catastrophic accident.

IV. Conclusion

This work demonstrates experimentally the results of thermal analysis via DSC performed in the laboratory, in computational simulations and through burning tests of rocket motors in a test bench. These results were essential for the shelf-life analysis of propellants based on HTPB / AP, objects of study of this work.

All the tests and experiments were carried out maintaining the highest degree of safety of the place and of personnel involved, having had the participation of several sectors including the Work Safety.

Based on the initial results of thermal analysis via DSC, it can be concluded that the Ea values acquired by propellants HTPB/AP with 11 years shelf-life were 126.67 kJ.mol^{-1} by the Ozawa method and 122.85 kJ.mol^{-1} by the Kissinger method,

so that they are well above the limit of those found in the literature (72.8 kJ.mol^{-1} and 79 kJ.mol^{-1}), and therefore, it is possible to state that, the rocket engines used and studied in this work containing composition of similar propellants, even after the period of validity of 10 years, are possible to carry out a possible extension study of its useful life.

The computational simulation, in turn, demonstrated the capacity of rearrangement of its molecules when subjected to a compressive force, causing the breaking of its original chemical bonds and allowing the emergence of other new chemical bonds.

The increase of these crosslinks, which in turn causes shrinkage in their volume, may be associated as a possible aging characteristic, which may lead to fractures and cracks of the propellant mass within a rocket motor. In this way, it has been demonstrated that the importance of a correct shelf life evaluation of its rocket engines, and otherwise, if used in real missions, could result in a catastrophic accident.

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