# ANALYSIS OF UNAGED AND AGED COMPOSITE ROCKET PROPELLANT FORMULATIONS BY FTIR AND SEM/EDX

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*Several rocket propellant formulations, based on hydroxyl terminated polybutadiene as a binder, were investigated before and after accelerated ageing. Ageing was performed isothermally between 65°C and 85°C. The influence of accelerated aging effect on solid fuel samples was studied by Fourier Transform Infrared Spectrometry and Scanning Electron Microscopy by X-ray scattering. The infrared spectrometric technique provided information regarding the effect of temperature on the functional groups belonging to the binder and the oxidant present in the investigated formulations. The SEM/EDX analyzes allowed the morphological investigation at a micrometric and submicrometric level of representative samples of material.*

**Keywords**: composite solid fuel, accelerated aging, FTIR, SEM/EDX

## 1. Introduction

The accelerating aging studies applied to the composite rocket propellants are a very useful tool which can decide how it will behave in time and how long can be used a solid rocket fuel, and for the existing ones, if the life of a solid rocket fuel can be extended or not. This paper contains a part of a unique national programme, that establishes the performance characteristics that must be met by a rocket fuel in order to be considered functional, and the static fire stand testing

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regarding their safe functionality, in this case, the rocket motor thrust and the burning stability [1, 2].

The main mechanism of aging in the composite rocket propellant is caused by the aging of the polymer matrix consisting of hydroxy terminated polybutadiene (HTPB). Based on the performed analysis, we aim to observe the physical and chemical transformation in the polymer matrix. Micro-cracks and morphological modification in the polymer can be observed by SEM while the FTIR can indicate oxidation reaction taking place or additional crosslinking in the chemical structure. These results alone, cannot be used for forecast, but considering the actual age of the propellant and by repeating the set of analysis in the future, after additional aging (natural or accelerated) a correlation can be made and a forecast could be estimated.

The oxidation potential of perchlorates is high, which makes this material suitable for high specific impulse fuels. The perchlorates are characterized by a $ClO_4^-$ anion in their molecular structure and are crystalline materials used in the formation of solid fuels. The size of the ammonium perchlorate (AP) particles and their shape influence the process of manufacturing the fuels and their burning rate [3, 4].

Because ammonium perchlorate does not contain metal atoms and the molecular mass of the combustion products is small, it is the most commonly used oxidant for solid rocket propulsion. The physical and chemical processes that can occur in the natural degradation process of composite fuels are related to the molecular reactions and diffusion phenomena governed by kinetic processes and can be accelerated by increasing the temperature [5, 6].

The paper presents studies performed by scanning electron microscopy and infrared spectrometry regarding the behavior of two solid fuel composite formulations based on ammonium perchlorate, HTPB and aluminum, under the effect of high temperature, in the range of 65-85°C, at regular time intervals.

Taking into account the investigation possibilities offered by the scanning electron microscopy and the specific nature of the investigated materials, the characteristic X-ray spectra were acquired on the basis of which the weight concentration of the chemical elements contained in the ammonium perchlorate material phase was expressed, in relation to aging parameters (time, temperature, humidity). The optimal scan current was determined so that the investigated samples are not degraded by electronic bombardment, a parameter that can damage the morpho-chemical structure by electrostatic charge and raise the investigation temperature and affect the chemical stability of the sample by favoring physical and chemical transformations, caused by the electric charge and temperature. Relevant conclusions were made regarding the dimensions of the oxidizing particles that enter the structure of the tested materials: perimeter, diameter, area, deviation from sphericity. Fourier transform infrared spectrometry

monitored the specific AP functional groups at the characteristic wavelengths. Prior to exposure to high temperature, the two solid fuel formulations were further investigated, so that the acquired data serve as reference elements in the monitoring process.

The combustion instability is governed by erosive burning phenomena or by abnormal development of the combustion front in the surfaces caused by cracking of the fuel. These two causes of combustion instability are a direct effect of propellant aging. So, by normal operation on bench firing, it can be demonstrated that the propellant has maintained its characteristics and structural integrity. It is very likely that these accelerated aging studies will predict the changes that occur in the stability, sensitivity, mechanical and functional properties of fuels, during their lifetime [7, 8, 9].

## 2. Experimental part

The investigated solid fuel compositions contain ammonium perchlorate as an oxidant, a fuel and a binder, with different proportions of additives. The unaged reference composition is assigned $T_0$. The compositions assigned PA01 and PA02 codes.

### *2.1. Method of accelerated aging*

Two compositions of ammonium perchlorate - based composite fuel containing different particle sizes of AP and different oxidant / fuel / binder ratios were studied. The purpose of the experiments was to study the effect of the high temperature on the oxidant and binder in these two solid fuel composite compositions. Accelerated aging was performed at varying temperatures and exposure times, as can be seen in Table 1. The accelerated aging temperature was chosen to a difference of 10°C. Thus, the stages of the accelerated aging process were carried out at 65°C, 75°C and 85°C, using a DY - Angelantoni climatic chamber, with a temperature controller programmable in the range - 40 ÷ + 180°C and humidity controller programmable in the rage of 4 ÷ 44 %. Fuel strips 5 x 50 mm in size were cut from the fuel samples and inserted into Duran - type glass vials, with a tight seal.

*Table no. 1.a*

**Accelerated aging conditions**

| Accelerated aging temperature [°C] | | |
|---|---|---|
| **65** | **75** | **85** |
| $T_0$ (reference) | | |

*Table no. 1.b*

**Accelerated aging conditions**

| Days of accelerated aging [day] | | |
|---|---|---|
| **24** | **17** | **7** |
| Measurement days | | |
| **PA01:** 2, 3, 6, 7, 8, 9, 15, 17, 20, 22, 24 | 1, 2, 4, 7, 8, 9, 10, 17 | 2, 3, 4, 5, 7 |
| **PA02:** 3, 6, 9, 15, 17, 20, 22, 24 | 1, 2, 4, 7, 8, 9, 10, 17 | 2, 3, 4, 5, 7 |

## *2.2. SEM/EDX and FTIR measurements*

**SEM / EDX.** In order to determine the experimental conditions of investigation of the two types of compositions, a series of tests were carried out in order to establish: (1) the behavior of electronic scanning, (2) to identify the material phases and to determine their elementary chemical structure, as well as (3) establishing the degree of morpho-structural degradation of the tested materials. In the test process, strips of material with dimensions of approximately 2 x 2 x 1 mm were used, so that the accumulation of electrical charge that could thermally degrade the material is minimised.

For each sample taken, quantitative determinations were made, which aimed to determine and quantify (relative and / or normalised) the elemental composition of the samples. In the case of qualitative micro-analysis, as well as in the case of quantitative micro-analysis, maps of relevant chemical elements were acquired, which led to the establishment of analytical relationships between the degree of degradation / aging, expressed by the mass percentages of the component elements and the chemical morpho-structure, in relation with aging parameters (time, temperature, humidity). In order to be able to determine the variations of the proportions of the chemical elements, induced to the investigated samples by the accelerated aging process, they were evaluated on the micro-surface, point and line, and will subsequently be compared with the experimental data acquired previously.

The investigation parameters of the samples by Scanning electron microscope VEGA II LMU equipped with a Bruker AXS X-ray scattering (EDX) microanalysis unit, which uses a QUANTAX 4000 X-ray radiation detector and an Xflash silicon drift (SD3) spectrometer. Operational parameters: voltage 30 keV; optimum scan current 20 ÷ 40 nanoamperes; 10 nm resolution, 50 x $10^{-2}$ Pa pressure.

**FTIR/ATR.** The solid fuel samples were analyzed and the peaks resulting from the IR analysis were assigned to the corresponding functional groups of AP, polybutadiene and plasticizer, based on the authentic reference substance and from the available bibliographic references.

The wavelengths attributed to the functional groups identified in the ammonium perchlorate molecule are: for the ammonium ion 1421 $cm^{-1}$ (1417 $cm^{-1}$ in the reference spectrum) and 3281 $cm^{-1}$ (3283 $cm^{-1}$ in the reference spectrum) and for the anion perchlorate 624.4 $cm^{-1}$ (623.4 $cm^{-1}$ in the reference spectrum), as can be seen in the Table 2.

*Table no. 2*

**The IR wavelength of the main functional groups that belong to the AP, polybutadiene and the plasticizer**

| Ammonium perchlorate | | | Polybutadiene | | | Plasticizer |
|---|---|---|---|---|---|---|
| $NH_4^+$ | $NH_4^+$ | $ClO_4^-$ | CH from -(CH=CH)- | C=C olefin | $CH_2$ near -(CH=CH)- | COOR |

| The wavelength of the spectrum of the analyzed material [$cm^{-1}$] | | | | | | |
|---|---|---|---|---|---|---|
| 3281 | 1427 | 625.3 | 969.7 | 1639 | 2846 | 1737 |

| The wavelength of the reference materials and from the specialty literature [$cm^{-1}$] | | | | | | |
|---|---|---|---|---|---|---|
| Ammonium perchlorate | | | Polybutadiene | | | Plasticizer |
| $NH_4^+$ | $NH_4^+$ | $ClO_4^-$ | CH from -(CH=CH)- | C=C olefin | $CH_2$ near -(CH=CH)- | COOR |
| 3283 | 1417 | 623.4 | 965 - 990 | 1580-1650 | 2870 - 2850 | 1750 -1735 |

The investigation parameters of the samples by FTIR / ATR. The monitoring of the functional groups characteristic of the ammonium perchlorate was performed with the help of an infrared spectrometer with Fourier transform FT-IR 6300, equipped with a single reflection diamond crystal (ATR). Operational parameters: wavelength between 4000 - 400 $cm^{-1}$; resolution 4 $cm^{-1}$; number of points / acquisitions: 3630; angle of incidence of 30°.

## 3. Results and discussions

In the case of formulation no. 2, sample code PA02, the chemical elements C, N, O, Al, and Cl were identified, with an approximate mass percentages of C : N : O : Al : Cl = 5 : 5 : 60 : 20 : 10. Ammonium perchlorate appears to be

embedded as a distinct material phase (Fig. 1.a and 1.b), having dimensions between 250 μm and 1 μm and aluminum particles between 10 μm and 0.1 μm.

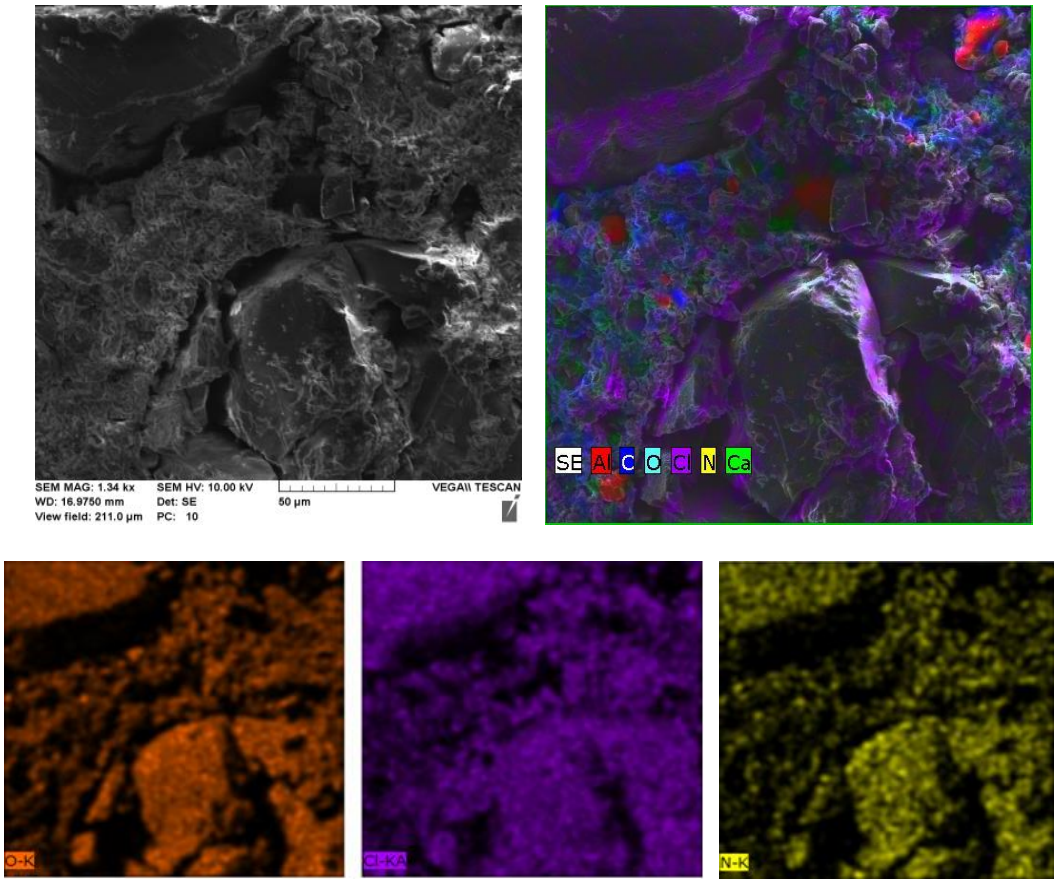
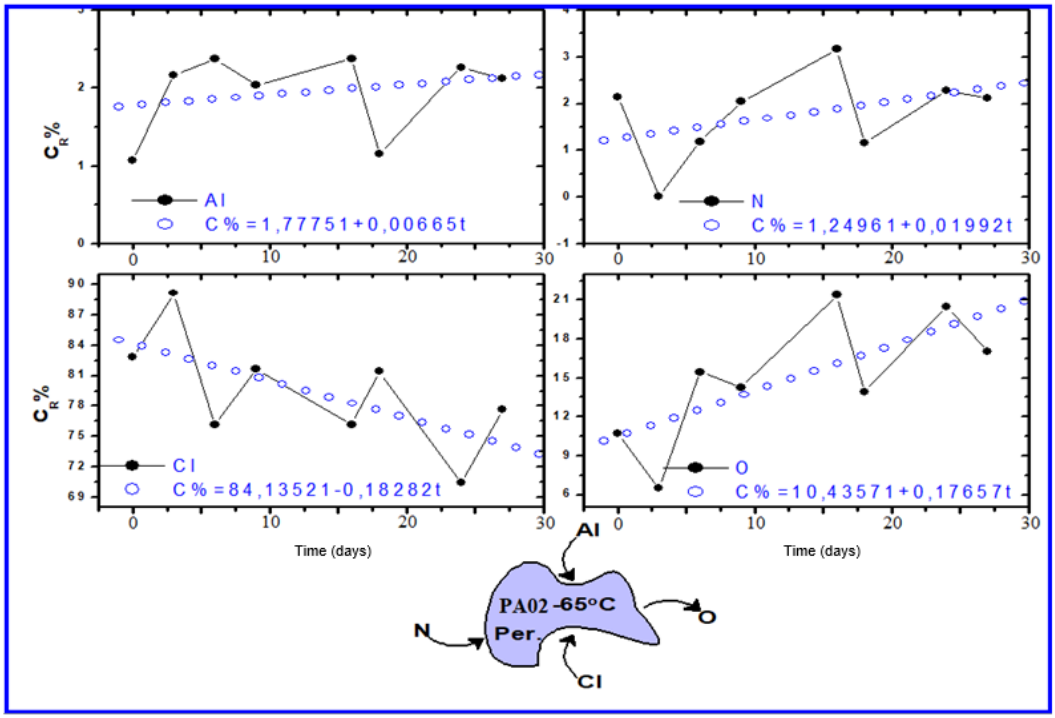
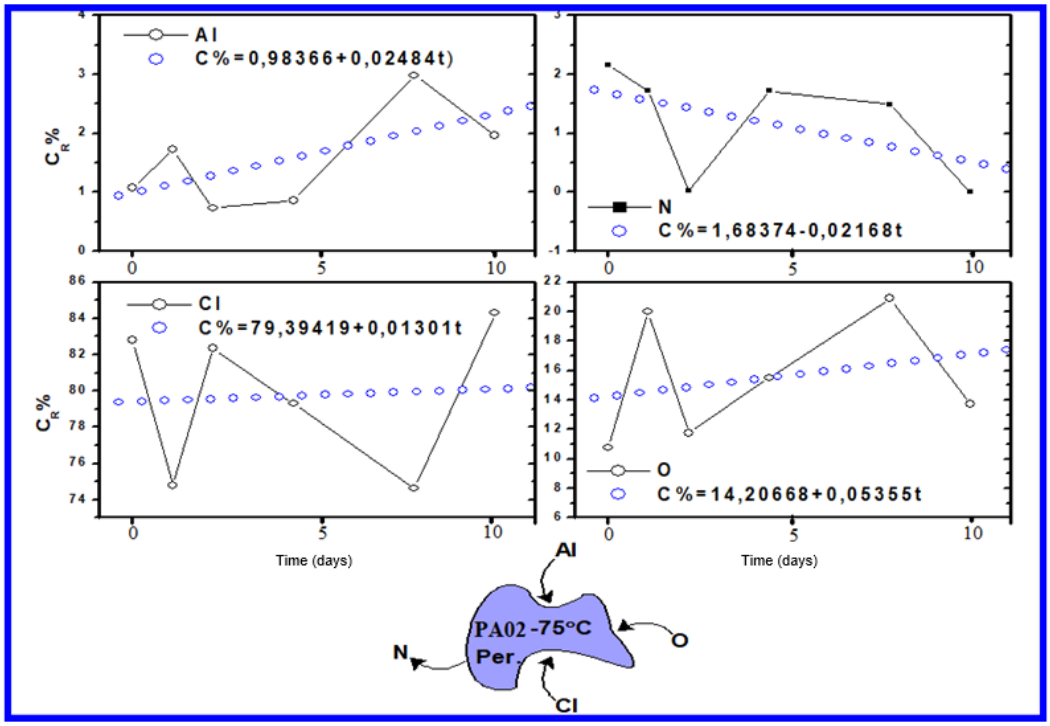



Fig. 1 Morphology and morpho-structure of the AP02 composition

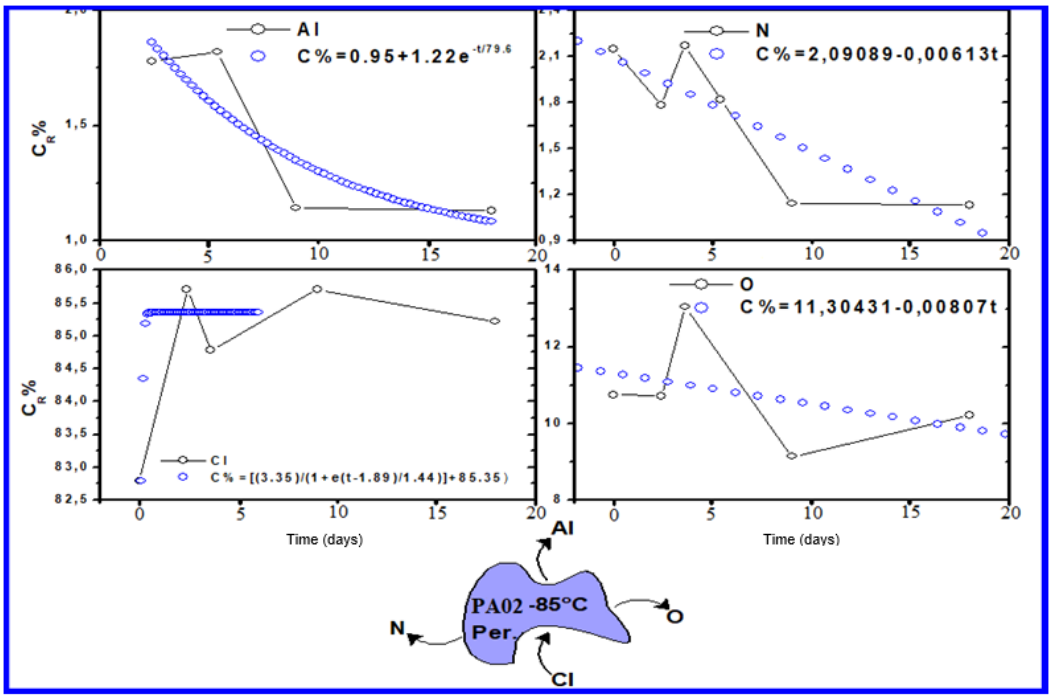
The variation of the chemical elements content in the structure of the material phase with the majority content of ammonium perchlorate, at the temperature of 65°C, 75°C and 85°C is shown in the Fig. 2.


Al
C % = 1,77751 + 0,00665t
N
C % = 1,24961 + 0,01992t
Cl
C % = 84,13521 - 0,18282t
O
C % = 10,43571 + 0,17657t
C_R %
Time (days)
PA02 -65°C
Per.
Al
N
O
Cl

a.


Al
C % = 0,98366 + 0,02484t)
N
C % = 1,68374 - 0,02168t
Cl
C % = 79,39419 + 0,01301t
O
C % = 14,20668 + 0,05355t
C_R %
Time (days)
PA02 -75°C
Per.
Al
N
O
Cl

b.




c.

| Day of accelerated aging | $C_R$ (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Al | C | N | Cl | Ca | Ni | Cu | O |
| 0 (Ref.) | 1.07 | - | 2.15 | 82.79 | 1.07 | 1.07 | 1.07 | 10.75 |
| 3 | 2.17 | - | - | 89.13 | - | - | 2.17 | 6.52 |
| 6 | 2.38 | 1.19 | 1.19 | 76.19 | 2.38 | - | 1.19 | 15.47 |
| 9 | 2.04 | - | 2.04 | 81.63 | - | - | 0 | 14.28 |
| 15 | 2.38 | - | 3.17 | 76.19 | - | - | 0.8 | 21.42 |
| 17 | 1.16 | 1.16 | 1.16 | 81.39 | - | - | 1.16 | 13.95 |
| 22 | 2.27 | 2.27 | 2.27 | 70.45 | 2.27 | - | - | 20.45 |
| 24 | 2.12 | - | 2.12 | 77.65 | 1.06 | - | - | 17.02 |

Fig. 2. Variation of the content of chemical elements in the structure of the material phase with a majority content of ammonium perchlorate at (a) 65°C, (b) 75°C, (c) 85 °C

The comparative evolution of the AP, binder and plasticizer through the main functional groups, of the unaged and aged PA02 solid fuel composite, are presented in Figs. 3-5.

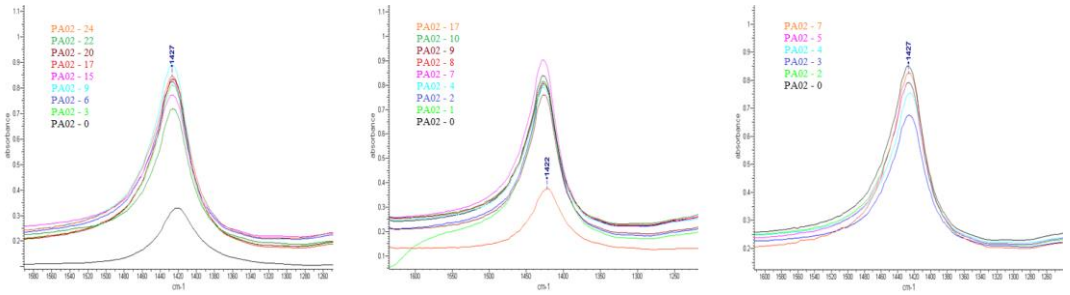



Fig. 3. IR microspectra of the $ClO_4^-$ anion group, wavelength 625.3 $cm^{-1}$, from ammonium perchlorate, and for the functional group CH from -(CH=CH)-, wavelength 969.7 $cm^{-1}$, from polybutadiene, accelerated aging process 65°C (left), 75°C (middle), 85°C (right) - PA02

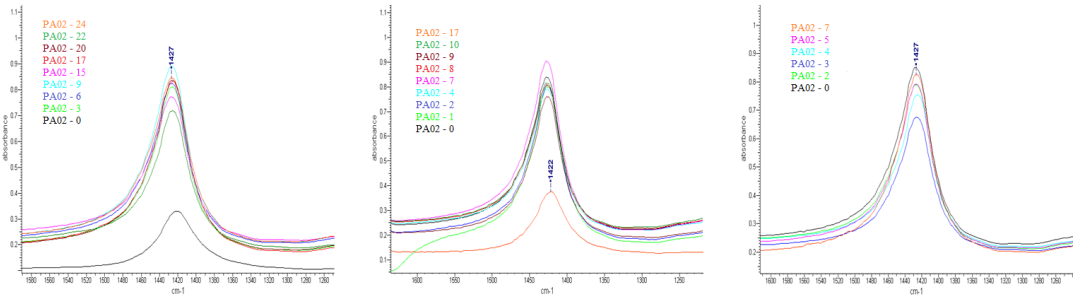



Fig. 4. IR microspectra of the $NH_4^+$ ion group, wavelength 1427 $cm^{-1}$, from ammonium perchlorate, accelerated aging process 65°C (left), 75°C (middle), 85°C (right) - PA02

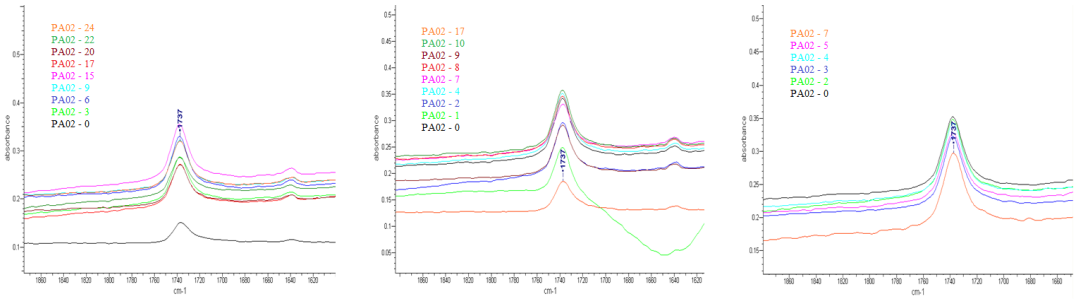



Fig. 5. IR microspectra of the *COOR* functional group from the plasticizer, wavelength 1737 $cm^{-1}$, accelerated aging process 65°C (left), 75°C (middle), 85°C (right) - PA02

## 4. Conclusions

The accelerating aging studies applied to the composite solid fuels have a very important role in extending the life time of a solid rocked fuel and to apreciate their behavior in time. The results presented in this paper will serve as a reference basis in a comparative analysis with the solid fuels aged in the coming years. For this, two solid fuel composite formulations, coded PA01 and PA02, were characterized through the effect of the high temperature on the main components, by FTIR and SEM/EDX. Over 24 days at a temperature of 65°C,

17 days of 75°C, and 7 days of 85°C, the ammonium perchlorate and polybutadiene based solid fuel formulations, have shown good chemical stability, without undergoing a morpho-structural degradation, and without micro-cracks.

No structural changes were observed on the aged samples, the functional groups corresponding to the compounds of interest - ammonium perchlorate, polybutadiene and plasticizer – have not changed in IR wavelengths compared to those investigated initially, unaged samples. By SEM / EDX monitoring, the chemical elements in the fuel mass exhibit a migration behavior between the material phases.

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