# New Solvent-free Polyurea Binder for Plastic Pyrotechnic Compositions

**GABRIELA TOADER[1,2], TRAIAN ROTARIU[1]*, EDINA RUSEN[2], JEREMIE TARTIERE[3], SORIN ESANU[1], TEODORA ZECHERU[4], IZABELA CRISTINA STANCU[2], ANDRADA SERAFIM[2], BOGDAN PULPEA[1]**

[1]Military Technical Academy, 39-49 George Cosbuc Blvd., 050141, Bucharest, Romania

[2]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Advanced Polymer Materials Group (APMG), 1-7 Gh. Polizu Str., 011061, Bucharest, Romania

[3]ENSTA Bretagne, 2 rue F. Verny, 29806 Brest Cedex 9, France

[4]Scientific Research Center for CBRN Defense and Ecology, 225 Oltenitei Road, 041309 Bucharest, Romania

The paper describes *the investigations related to the fabrication and characterization of two new plastic pyrotechnic compositions using solvent-free polyurea as binder. These solvent-free polyurea binders allow wet or dry pressing of the pyrotechnic compositions. The rubbery texture of the polyurea binders minimize the risks associated to the dry pressing of other brittle binders. A comparative theoretical and experimental study between these new types of binders and a conventional binder has been performed, in order to establish the improvements that could be brought to the pyrotechnic compositions, in terms of safety and performance.*

*Keywords: polyurea, solvent free, binder, malleability*

Pyrotechnic compositions are mechanical mixtures of substances that when ignited, undergo an energetic chemical reaction at a controlled rate intended to produce on demand and in various combinations, specific time delays or quantities of heat, noise, smoke, light or infrared (IR) radiation [1]. The main use of civilian pyrotechnics includes explosive systems like fireworks, airbags, flares and fire extinguishing charges. Military pyrotechnics have also numerous applications, including tracers, illuminating candles, incendiary devices, smoke generators for signaling or Vis/IR obscuration, delay fuses, counter-measurement flares and primers. Because of their energetic nature (violent generation of heat and hot reaction products) and taking into account that they are often used by an operator, the proper and consistent functioning of a pyrotechnic device can be the difference between life and death.

There are many components of a pyrotechnic mixture: oxidizers, fuels, binders, dyes and other additives, and these are generally mixed in powdered form when they are loaded in the pyrotechnic systems. The loading process consists in pressing the granular mixture into a mold followed by its introduction in other assemblies or directly pressing it in the assemblies' bodies.

Typical pyrotechnic compositions contain around 10% of a natural or artificial hard polymeric binder that is compacted to a dense solid by molding in a die. The binders that are commonly used in pyrotechnics are natural polymers (starch, Arabic Gum) or synthetic resins (Shellac, Novolac) or synthetic polymers (nitrocellulose). The conventional manufacturing process for a pyrotechnic mixture implies the dissolution of the polymer in a solvent (ethylic alcohol, isopropyl alcohol, ethyl acetate, acetone) the addition of the lacquer to the mixture of solid components, the granulation and finally the removal of the solvent. The granular composite is then pressed at elevated pressures in metallic dies or directly in pyrotechnic device cases.

These conventional technologies described above imply many hazards associated to the use of a volatile and flammable solvent for the preparation of an explosive material, as well as the use of high pressures and metallic dies to load extremely sensitive materials. The environmental burden is also of importance because of the inherent VOC emissions.

In this context, what is proposed here is to investigate the possibility of developing a modern polyurea-based binder (cross-linked pre-polymers) and a die-cast load process. This method is effective for the manufacture of dense rigid pyrotechnic charges having a specific geometry. Polyurea is an elastomeric polymer that can be obtained by a rapid polyaddition reaction between a diamine and a diisocyanate [2-3]. Polyurea usually presents a rubber-like texture, with high humidity resistance, it cures [4] within a few hours without catalyst and it is a homogenous non-porous material, as polyurethanes. For pyrotechnic compositions, the use of a polyurea binder brings important advantages: it consists in a single step mixing process; the liquid reagents allow easy mixing of the whole composition, there are no volatile and flammable solvents needed for the mixing; there are no VOCs resulting from the process; the loading stage imply the use of low pressures and non-metallic dies drastically diminishing the risk of accidental initiation.

Another advantage brought by polyurea versus polyurethanes, consists in a lower exothermic effect during synthesis, which guarantees safety in this particular case, when it is used with the pyrotechnic compositions. Polyurea also has the benefit of not forming pores/gas bubbles during the synthesis process, like it happens in the case of polyurethanes, which affects the pyrotechnic compositions combustion process.

This paper describes a new type of elastomeric polyurea binders, which aim to join its excellent properties with the safety and performance requirements for the pyrotechnics. The hard nanodomains [5] of this material and its cross-linked structure [6] ensure an improved mechanical resistance of the pyrotechnic compositions, which turns into low sensitivity to impact and friction while the homogeneity and the low moisture content ensure a good performance. The aliphatic reagents used for the synthesis

* email: traian.rotariu@gmail.com, Phone: +40213364591

of these new binders (polyetherdiamine and isophorone diisocyanate) also ensure UV stability [7].

## Experimental part

*Materials and methods*

Barium nitrate ($Ba(NO_3)_2$, Sigma Aldrich), magnesium (Mg, powder, Sigma Aldrich), barium peroxide ($BaO_2$, Sigma Aldrich), poly(propylene glycol)bis(2-aminopropyl ether) - Mn≈2000 Da (PPG2000, Sigma Aldrich), poly(propylene glycol)bis(2-aminopropyl ether) - Mn≈4000 Da (PPG4000, Sigma Aldrich), triethylenetetraamine (TETA, Sigma Aldrich), Isophorone diisocyanate (IPDI, Sigma Aldrich), polyvinyl chloride (PVC, powder, Oltchim S.A.), phenol-formaldehyde resin (Iditol, UM Sadu Gorj), priming composition (based on barium peroxide and magnesium, Military Technical Academy) and ethanol (Sigma Aldrich) were used as received.

Preparation of the pyrotechnic compositions

The pyrotechnic compositions were obtained by following several mandatory steps: ingredients drying; granulometric sorting; dry mixing; lacquer preparation (for Iditol binder); wet mixing (for Iditol binder); partial drying; granulation; final drying and pressing.

The first step consisted in the granulometric sorting of the solid components ($Ba(NO_3)_2$, $BaO_2$, Mg and PVC). Only the 200 μm fractions were used further.

The classical pyrotechnic composition using Iditol binder was prepared by mixing the solid components with the resin (50% ethanol solution), passing them through a sieve and allowing them to stay for 72 h at 60°C.

The pyrotechnic compositions using polyurea binder were obtained in two stages: firstly TETA and PPG (PPG2000 or PPG4000) were mixed with the solid components, then IPDI was added and the mixture was stirred vigorously. The whole mixture was passed through a sieve and cooked in oven for 72 h at 60°C.

With the aim of studying the combustion and mechanical properties, cylindrical charges (fig.1) containing 2 g of each pyrotechnic composition were obtained using a metallic mold (10 mm inner diameter).

(a) (b)

Fig. 1. Cylinders of pyrotechnic compositions: (a) PC1_P; (b) PC1_P (right), PC2_P (down), PC3_P (left)

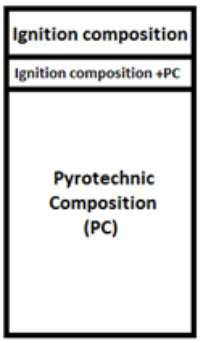


Fig. 2. Schematic illustration of the pyrotechnic composition cylinders

The dried pyrotechnic mixtures were pressed with a hydraulic press (PC1_P, PC2_P and PC3_P).

For the combustion tests, a small quantity of priming (ignition) composition was placed on the top of each cylinder before the pressing process, as illustrated in figure 2.

In order to demonstrate that the compositions containing polyurea can be pressed by hand, wet pressing was performed using the same mold and the cylinders (PC2_H and PC3_H) were then allowed to dry for 72 h at 60°C. Hand pressing consisted of placing a load of 10 kg on the mold, in order to have the same loading pressure for all the samples.

The reagents ratios in the composition for each pyrotechnic mixture is presented in table 1.

Characterization

In order to evaluate the safety and performance characteristics of the synthesized pyrotechnic compositions, various analyses were performed.

The thermal behavior and the stability of the pyrotechnic mixtures were analyzed through Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). An OZM 551 Ex Differential Thermal Analysis System was used and the samples (25-30 mg) were heated from 30 to 450 °C, with different heating rates: 10 °C/min, 15 °C/min, 20 °C/min and 25°C/min. DSC was performed using a Perkin Elmer PYRIS Diamond DSC instrument. Samples having 2-5 mg were heated from 30 to 450 °C with different heating rates: 5, 7.5, 10 and 12.5 °C/min.

The pyrotechnic compositions were also subjected to the thermal vacuum stability test, which consists of artificial aging of 5 g of sample at 100 °C for 40 h [8]. Their chemical stability is reported as volume of gases released per grams of sample.

The heat of combustion was evaluated using an AVL Ballistic instrument (calorimetric bomb). For this measurement, 2 g of each sample were initiated in a closed vessel using a hot wire. The specific volume of the gases released from the calorimetric bomb was measured using a Julius Peters gas-meter.

**Table 1**

COMPOSITION OF THE PYROTECHNIC MIXTURES

| Component | Oxidant | | Fuel | Additive | Binder | | |
|---|---|---|---|---|---|---|---|
| Composition | $Ba(NO_3)_2$ [%] | $BaO_2$ [%] | Mg [%] | PVC [%] | Iditol [%] | Polyurea (PPG2000) [%] | Polyurea (PPG4000) [%] |
| PC1_P | 55 | 10 | 15 | 10 | 10 | - | - |
| PC2_P | 55 | 10 | 15 | 10 | - | 10 | - |
| PC3_P | 55 | 10 | 15 | 10 | - | - | 10 |
| PC2_H | 55 | 10 | 15 | 10 | - | 10 | - |
| PC3_H | 55 | 10 | 15 | 10 | - | - | 10 |

For the burning experiments, a video camera, a lux meter and a thermal camera were used in order to evaluate the behavior of the pyrotechnic composition. For each composition, five measurements were performed and the average value was reported.

The burning rates of the pyrotechnic compositions were calculated by dividing the length of the cylindrical charges by the duration of their combustion, according to eq. (1):

$$v_c = l/\Delta t, \quad (1)$$

where: $v_c$ = burning rate, l = length of the cylinder, $\Delta t$ = duration of the combustion.

The intensity of the light resulted during the combustion experiments was calculated by multiplying the illuminance (measured with the luxmeter) with the square of the distance between the instrument and the cylinders, according to eq. (2):

$$I = E \cdot R^2, \quad (2)$$

where: I = light intensity, E = illuminance and R = distance between the instrument and the cylinders.

The temperature of the flame generated during the pyrotechnic compositions combustion was measured with a thermal camera.

The moisture content of the pyrotechnic mixtures was measured using an Axis Thermobalance. For this analysis, 5 g of sample were heated at 100 °C for 2 h, and weighted every 150 s. For each composition, three measurements were performed and the average value was reported.

The mechanical properties of the synthesized materials have been evaluated using a Brookfield CT3 texture Analyzer, equipped with a 4500 g cell and a TA4/1000 compression accessory. The tests were performed at room temperature, at a compression rate of 1 mm/s. The cylinder-shaped samples were compressed up to a strain of 90%. In order to obtain relevant results, five specimens of each composition were compressed and a compressive stress-strain diagram was plotted.

The impact sensitivity of the pyrotechnic compositions was evaluated using the Kast fall hammer instrument. In order to perform this measurement, 25 mg of sample were placed between two metallic cylinders fixed in a bigger metallic ring and then placed on a metallic support as illustrated in figure 3.

The sensitivity to impact was evaluated as the energy (height multiplied with the gravity of the hammer) necessary to initiate 50% of the samples.

The friction sensitivity was determined using a BAM Friction sensitivity instrument. The compositions were placed between a ceramic cylinder and a ceramic plate which were passed one over the other while the apparatus applied various pressing forces. The friction sensitivity is determined as the minimum applied force that initiates 50% of the samples.

In order to evaluate also theoretically the chemical equilibrium compositions and the thermodynamic properties of the new pyrotechnic compositions, NASA software - CEA (Chemical Equilibrium with Applications) was used.

## Results and discussions

The synthesis of the two types of polyurea further used as binder in our pyrotechnic compositions is illustrated schematically in figure 4.

The introduction of TETA conducts to a cross-linked polymer network, which brings various advantages: a shorter reaction and curing duration, enhanced mechanical

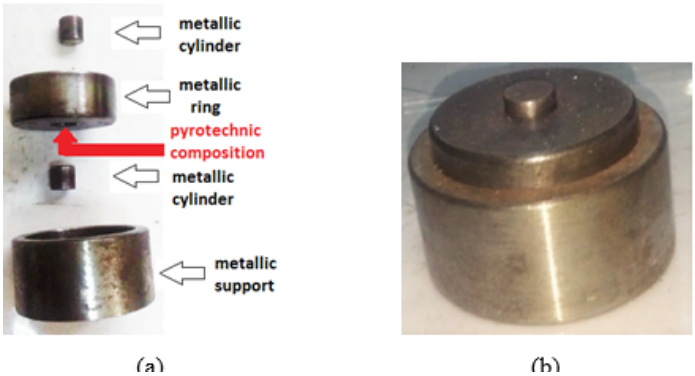


Fig. 3. Setup of the samples for the impact to sensitivity test: (a) disassembled; (b) assembled

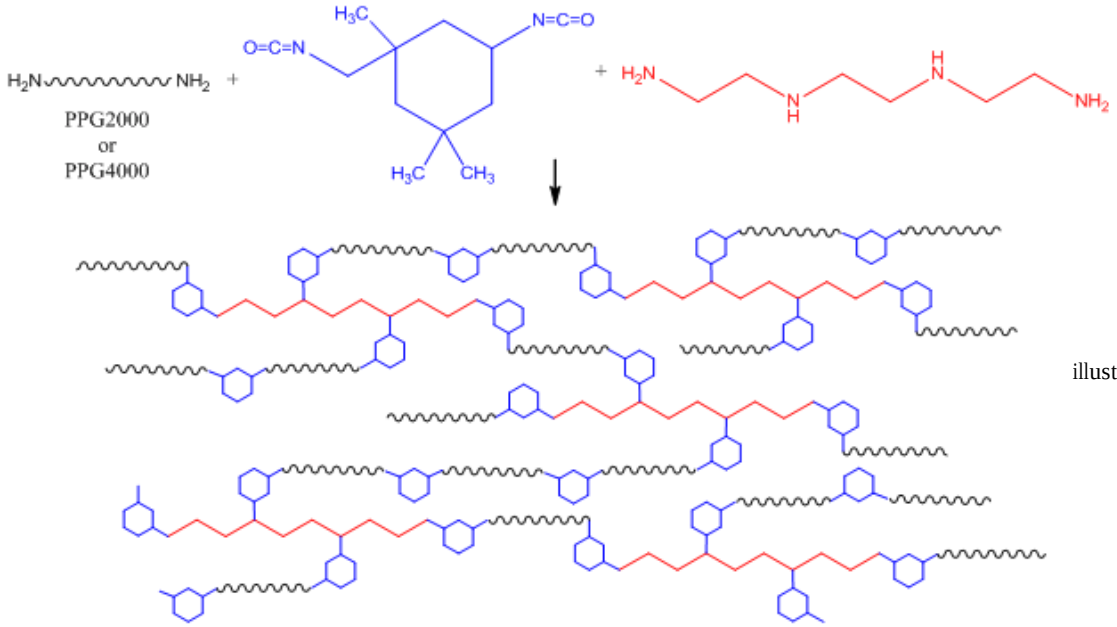


Fig. 4. Schematic illustration of the polyurea binder synthesis

| Parameter | PC1_P | PC2_P | PC3_P |
|---|---|---|---|
| **Combustion temperature - TTh.** [K] | 2750 | 3240 | 3250 |
| **Specific volume - $V_{0sp}$Th.** [l/kg] | 382 | 346 | 355 |
| **Heat of combustion - $Q_V$Th**[kcal/kg] | 750 | 683 | 697 |

**Table 2**
THEORETICAL EVALUATION OF THE THERMODYNAMIC CHARACTERISTICS

| Composition | Heat of combustion / Specific volume | |
|---|---|---|
| PC1_P | $Q_V$ [kcal/kg] | 702.6 |
| | $V_{0sp}$ [l/kg] | 365.6 |
| PC2_P | $Q_V$ [kcal/kg] | 644.9 |
| | $V_{0sp}$ [l/kg] | 308.5 |
| PC3_P | $Q_V$ [kcal/kg] | 670.4 |
| | $V_{0sp}$ [l/kg] | 370.8 |

**Table 3**
EXPERIMENTAL RESULTS OBTAINED FOR THE HEAT OF COMBUSTION AND SPECIFIC VOLUME

properties and moisture resistance. The difference between the polyurea obtained by employing PPG2000 or PPG4000 consists in the malleability of the polymer. Thus, polyurea synthesized with PPG4000 is more flexible due to the longer aliphatic chains from its structure. Depending on the application for which it is designed, PPG2000 or PPG4000 can be utilized according to the necessary final properties of the pyrotechnic compositions. For these reactions we used 80% (wt.) PPG and 20% (wt.) TETA. The molar ratio between the isocyanate groups and the amino groups was 1:1 in both cases, and it sould always have this value, even if the ratio between PPG and TETA may be different than here.

A theoretical study of the pyrotechnic compositions represents a prior stage in the development of a pyrotechnic composition, which provides information about their thermodynamic characteristics like heat of combustion and specific volume. The results obtained are illustrated in table 2.

These theoretical results can be related to the properties of the pyrotechnic composition and allow their primary evaluation. The experimental values obtained are presented in table 3.

The heat of combustion and specific volumes experimentally determined are in good agreement with the theoretical evaluations made using CEA software. From the analysis of data from tables 2 and 3, it is obvious that the polyurea-based compositions show slightly lower combustion heats and specific volumes, but they produce higher combustion temperatures, which is a very important feature for an illuminating composition, indicating that this material can provide good conditions for emission and excitation of the active species (barium chloride in this case) [3].

The loading density was calculated by dividing the pyrotechnic composition weight at the volume that is occupies after it is pressed and the average results are displayed in table 4.

The loading density influences the burning rate, but this value it is also influenced by the chemical composition, the dimensions of the particles and the confinement. The average values of burning rates, flame temperature and light intensity obtained during experiments are also presented in table 4.

**Table 4**
COMBUSTION EXPERIMENTS RESULTS

| Parameter | PC1_P | PC2_P | PC3_P | PC2_H | PC3_H |
|---|---|---|---|---|---|
| **Loading density – ρ** [g/cm$^3$] | 1.66 | 1.67 | 1.91 | 1.4 | 1.4 |
| **Burning rate – Vc** [mm/s] | 2.73 | 1.12 | 0.93 | 1.26 | 1.44 |
| **Flame temperature – T** [°C] | 1383 | 1520 | 1436 | 1378 | 1366 |
| **Light intensity – I** [lux· m$^2$] | 636 | 638 | 263 | 331 | 404 |

The cylindrical charges were burned in vertical and horizontal positions in order to evaluate if there are any differences. Charges burned horizontally showed slightly higher values. PC3_P is more flexible than PC2_P due to the longer aliphatic polyether chains in its structure; consequently, PC3_P has the highest loading density. Higher loading densities led to lower burning rates. Even if polyurea slows down the burning process, inducing lower burning rates, the pyrotechnic effect seems to be approximately the same as in the case of PC1_P. Therefore, for approximately the same effect, the combustion will last longer, and this could be an advantage in the performance of the pyrotechnic mixture.

The mechanical properties of the pyrotechnic compositions are closely related to the type of binder employed, but also to the loading density, size of particles, confinement or environmental conditions during mechanical tests [9].

All the types of pyrotechnic compositions prepared were subjected to compression tests in order to evaluate their mechanical properties.

The compression modulus was computed at 0.2% strain, and the average values were plotted (fig. 5, a). It is obvious that PC1_P is the most rigid composition, with a compression modulus of 1700 kPa. This mechanical behavior is confirmed also by the compressive stress-strain diagram (fig. 5, b), which indicates that the PC1_P samples were much more rigid than the other compositions. The fact that increasing the applied stress leads to an increased deformation for all the other samples, states for a rearrangement of their internal structure. PC2_P and PC3_P show higher values of the compressive modulus versus PC2_H and PC3_H, respectively (fig. 5, a). The difference between the samples pressed with the hydraulic press (PC2_P and PC3_P) and the ones pressed by hand (PC2_H and PC3_H) is also noticeable in figures 5, b and Figure 5, c. PC2_H and PC3_H have a more compact structure, which allows them to deform, but not to break when higher stress is applied.

An important aspect regarding the safety of the pyrotechnic mixtures is represented by their thermal sensitivity and thermal stability. The thermal behavior of the pyrotechnic compositions was studied by means of DTA and DSC analysis. DTA showed that PC1 is stable up to approximately 270°C and PC2 and PC3 up to approximately 240°C. The decomposition temperature (temperature sensitivity) varies according to the heating rate of the sample, as illustrated in table 5. It can be noticed that the pyrotechnic compositions containing polyurea present a similar thermal behavior and they start the decomposition process earlier than PC1, due to the fact that they have a higher content of aliphatic chains in their structure.

The DSC analysis provided more accurate values of the decomposition temperatures. The results are displayed in table 6.

The DTA and DSC results are in good correlation, showing similar values for the self-ignition temperature. It can be noticed that when the heating rate increases, the decomposition temperature increases too [10]. It is very important to know these values in order to establish which should be the safety measures that must be taken into account for these new pyrotechnic compositions.

Another analysis that can provide information about the thermal stability of these materials is represented by the vacuum stability test. If the pressure increases considerably, it means that the material is unstable and generates a high quantity of gaseous products. The new

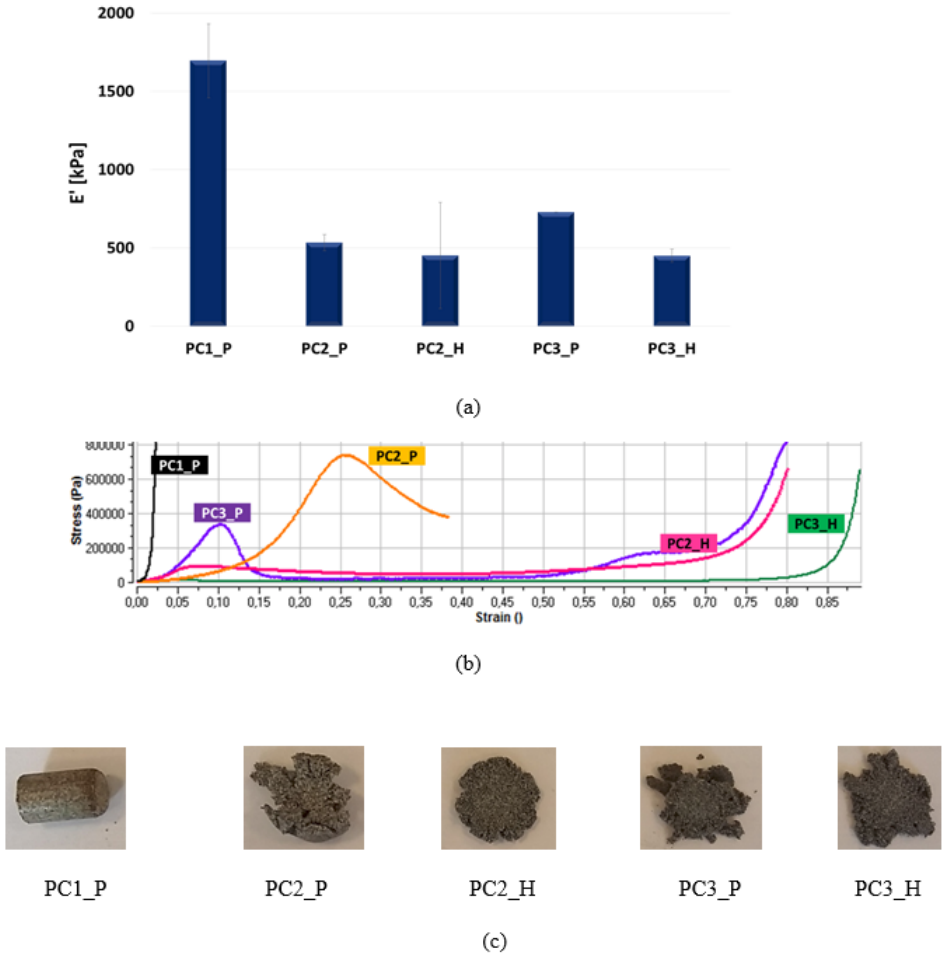


Fig. 5. Compression tests on the compositions: (a) Average values of the compressive modulus (E' [kPa]); (b) Compressive stress-strain diagram; (c) Digital photographs of the compressed samples

| Heating rate [°C/min] | PC1 decomposition temperature [°C] | | | PC2 decomposition temperature [°C] | | | PC3 decomposition temperature [°C] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Start | Onset | Top | Start | Onset | Top | Start | Onset | Top |
| 10 | 237 | 262 | 269 | 201 | 231 | 238 | 198 | 223 | 239 |
| 15 | 230 | 269 | 277 | 180 | 236 | 244 | 206 | 229 | 246 |
| 20 | 235 | 273 | 282 | 174 | 243 | 253 | 205 | 233 | 249 |
| 25 | 237 | 279 | 291 | 205 | 251 | 260 | 204 | 238 | 256 |

**Table 5**
DTA RESULTS FOR THE PYROTECHNIC COMPOSITIONS

**Table 6**
DSC RESULTS FOR THE PYROTECHNIC COMPOSITIONS

| Heating rate [°C/min] | PC1 decomposition temperature [°C] | PC2 decomposition temperature [°C] | PC3 decomposition temperature [°C] |
|---|---|---|---|
| 5 | 263.6 | 237.3 | 244.6 |
| 7.5 | 273.0 | 244.0 | 252.0 |
| 10 | 275.1 | 250.9 | 253.0 |
| 12.5 | 280.9 | 261.8 | 256.0 |

pyrotechnic mixtures released an insignificant quantity of gaseous products during tests: while PC1 has a specific volume of 0.934 $cm^3/g$, PC2 and PC3 have 0.625 $cm^3/g$ and 0.361 $cm^3/g$ specific volumes, thus showing a much better stability versus PC1.

In terms of safety, there are two other tests that are usually performed on the pyrotechnic materials: sensitivity to impact and sensitivity to friction. The impact sensitivity provides information about the minimum energy required to initiate the decomposition of an energetic material. The average values of these energies for the pyrotechnic compositions are: 33 J for PC1, 40 J for PC2 and 36 J in case of PC3. The rubbery texture of the polyurea binder, which covers the solid particles of these pyrotechnic compositions, requires a higher energy for the ignition of these materials; therefore, they are less sensitive to impact than PC1.

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The same behaviour was observed during the friction sensivity tests, when there were no ignitions observed, even with the highest load, corresponding to 350N.

The moisture content of the pyrotechnic compositions is a parameter that influences the performance of these materials. PC2 (0.13% moisture) anc OPC3 (0.27% moisture) have a lower content of humidity than PC1 (1.8%) due to the high hydrophobic charcater of polyurea.

## Conclusions

New types of solvent-free binders were employed in pyrotechnic compositions and they were compared with a classical solvent-based binder. One-step preparation process, ease of reagents mixing, fast curing, homogeneity (no pores, voids or cracks), lower sensitivity, lower higroscopicity, are a few of the advantages brought by a polyurea binder.

The safety and performance characteristics of these compositions were evaluated by performing tests and analyses specific to pyrotechnic compositions: burning experiments, thermodynamical and thermal analysis, thermal vacuum stability, compression tests, sensitivity to impact, sensitivity to friction and moisture content.

These compositions were designed to generate a green color flame and it seems that the values obtained from these analyses fulfill the requirements of this type of materials.

Combustion experiments showed that polyurea binders slow down the burning rate, maintaining meanwhile the flame temperature and the light intensity; thus, the same effect can be obtained for a longer period of time. Thermal analysis and vacuum stability tests revealed that the polyurea-containing pyrotechnic mixtures are stable at temperatures above 200 °C. They also proved to have lower sensitivity to impact and friction. The compression

measurements showed that their mechanical behavior varies with their texture (rigid or flexible polyurea).

The advantage is that polyurea binder brings a series of advantages in terms of safety and performance and this material can be successfully employed in pyrotechnic compositions, and further, these new pyrotechnic compositions may be designed according to the type of application for which they are manufactured.

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