Theoretical and Experimental Studies on New Plastic Pyrotechnic Compositions

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The aim of this research is to develop plastic pyrotechnic compositions with a high level of moldability while maintaining safety and performance features specific to usual plastic bonded pyrotechnic compositions. In this view, theoretical and experimental studies have been performed in order to determine the characteristics of three new plastic pyrotechnic compositions and to establish their agreement with energetic materials safety and performance essential principles. These formulations have been designed to accomplish special requirements, such as processing performances, i.e. good malleability for hand packing or molding at room temperature, and pyrotechnic effects, i.e. illuminating or smoke signaling.

Keywords: red phosphorus, malleability, processing

Pyrotechnic compositions are mechanical mixtures containing minimum two readily-oxidizable and readily-reducible compounds that, under the action of an external stimulus undergo a chemical reaction of combustion releasing solid, liquid and gaseous products at high temperatures, generating in the same time pyrotechnic effects: bright light, colored light, smoke or infrared radiation [1-2], useful in various military or civilian applications. The pyrotechnic mixtures easily ignite by flame, and develop burning rates of mm/s order, releasing high amounts of heat (thousands of J/g) and elevated temperatures of the reaction products (thousands of K) [3]. Usually, there are many components of a pyrotechnic mixture (oxidizer, fuel, binder and additives) and these are generally utilized in powdered form when they are loaded in the pyrotechnic systems (by pressing them into a mold followed by their introduction in other assemblies or direct pressing in the assemblies bodies), but they also can be turned into liquid state and casted in the assemblies bodies.

The geometry and the dimensions of the pyrotechnic mixtures are designed to accomplish specific performances regarding the time of combustion, light intensity, smoke density or other parameters that define a certain pyrotechnic effect. The geometry and the dimensions of a pyrotechnic system are determined by specific values, such as combustion surface, burning rate and time of combustion. The combustion surface and the burning rate are dependent on the chemical composition of the pyrotechnic mixture and on the loading parameters [3–5].

In order to safely store, transport, operate and utilize pyrotechnic compositions, the following conditions must be also fulfilled: an uniform combustion and a well-defined burning rate for all environmental conditions; a good physical and chemical stability; an adequate sensitivity and a low reactivity under the action of mechanical, thermal or electrical stimuli; low explosive profile and low risk of accidental initiation; low risk of generating toxic reaction products [6-7]; easy, efficient and economic production technology.

Typical pyrotechnic compositions contain around 10% of a natural or artificial hard polymeric binder and are compacted to dense solids by molding. A modern option is the use of polyurethane binders (cross-linked pre-polymers) and a die-cast load process. Both of the methods are effective for the manufacture of dense rigid pyrotechnic charges having a specific geometry.

In the case of plastic pyrotechnic compositions, besides the general requirements presented above, there are some specific requirements, such as good malleability and plasticity, and having a texture similar to modeling clay, allowing hand packing in variable geometry, thickness, length and combustion surface. Plastic mixtures, known as plastic bonded explosives (PBXs), are extensively used in military applications due to their high safety, processing ease and superior strength [8-9]. To the best of our knowledge, the only energetic materials manufactured to be packed/ hand molded, using plastic binders are the high explosives [8]. Besides the major component (the explosive), they also contain a polymeric binder, plasticizers and stabilizers. A very important characteristic of a plastic explosive is represented by the possibility of being molded and adjusted at the time of its use, possessing this way a wide range of possible applications. Polymeric binders and plasticizers also have an important role in reducing sensitivity to hazardous stimuli such as shock, friction or impact [8-14].

This paper presents the results of the theoretical and experimental studies regarding three novel plastic pyrotechnic compositions designed for signaling with colored flame and smoke. These pyrotechnic compositions have a specific design, presenting a high malleability induced by the binder system, which allows them to be hand-packed or molded into any geometric shape and to obtain this way different combustion thicknesses and surfaces. Upon ignition, they also generate pyrotechnic effects with performances and combustion durations specific to conventional signaling pyrotechnic compositions.

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Component	Oxidant			Fuel		Additive	Binder
Composition	Sr(NO₃)₂	Ba(NO₃)₂	KNO₃	Mg	P	PVC	Binder
PC-1	60	-	-	15	-	15	10
PC-2	-	62	-	10	-	15	13
PC-3	-	-	66	-	27	-	7

Table 1
COMPOSITION OF THE PYROTECHNIC MIXTURES

Experimental part
Materials and methods
Strontium nitrate, barium nitrate, potassium nitrate, magnesium (powder, 0.2 mm), red phosphorus were purchased from Sigma Aldrich, polyvinyl chloride (powder) from Oltchim S.A. were used as received, and a nitrile-butadiene rubber-based binder containing 3% wax and 4% dioctyl-phthalate in methylene chloride made by the Scientific Research Center for CBRN Defense and Ecology was freshly prepared.

Preparation of the pyrotechnic compositions
A pyrotechnic effect is generated as the result of the interaction between combustion reaction products and environment. Therefore, the pyrotechnic mixture should be designed to obtain reaction products with specific chemical compositions, temperatures and emission flows. The compositions of the pyrotechnic mixtures are presented in table 1. The main criteria for the design of PC-1 and PC-2 compositions is represented by a minumum of metallic fuel in order to obtain a low burning rate, followed by the introduction of a plasticizer in the binder to ensure the pyrothechnic composition maleability and the additive introduction in order to obtain an appropriate coloured flame. For the smoke composition PC-3, oxidant and fuel ratios were established in such way to achieve a high combustion rate and maleability.

After choosing the chemical composition and the pyrotechnic mixtures manufacture, the next step consisted in the design of the pyrotechnic load, when various parameters were established by calculus or experimental trials: geometric characteristic (diameter, thickness, area, volume); physical characteristics of loading (pressure, pressing time, column height, confinement); interactions between the pyrotechnic compositions and other elements of the pyrotechnic system/ammunition, such as the ignition or the reaction products release method.

Characterization
The mechanical properties of the pyrotechnic compositions have been assessed according to ASTM D695, using a Brookfield CT3 Texture Analyzer, equipped with a 4500 g cell, using a 1 mm/s compression rate. The specimens were cut into cylinder-shape samples, whose length was twice as the diameter (L/D = 20 mm / 10 mm) and conditioned at 23 ± 2° C prior to testing. Five specimens were used for each composition and they were compressed up to a strain of 99%.

The safety and performance characteristics depend on various parameters, such as physical properties (maximum density, loading density), chemical properties (chemical composition, humidity), thermodynamic properties (heat of combustion, temperature, burning rate, specific volume), sensitivity (impact, friction, self-ignition).

In order to establish the agreement of these new pyrotechnic compositions with the safety and performance essential principles, theoretical and experimental studies were performed.

For the theoretical study, chemical equilibrium compositions and thermodynamic properties were deduced by means of a NASA software, CEA (Chemical Equilibrium with Applications). The heat of combustion is a major factor influencing the thermodynamic characteristics, the performance and the effect of pyrotechnic compositions, therefore an AVL Ballistic instrument (calorimetric bomb) was used for determining the heat of combustion. The specific volume was calculated by measuring the pressure increase in a Julius Peters column, generated by the gaseous reaction products resulted from the calorimetric bomb.

In order to assess the thermal mass flow and combustion rate interdependence, loading density was calculated. After weighing approximately equal quantities of pyrotechnic composition, cylinders of 10 mm diameter were obtained by manually pressing them in a metallic mold. After measuring the dimensions of the pyrotechnic composition cylinders and their combustion time, the burning rate was calculated.

The thermal stability of the pyrotechnic compositions was analyzed by means of a DTA OZM 551 Ex Differential Thermal Analysis System provided with specialized software Meavy. The tests were performed on 25-30 mg of sample heated between 20-450°C with a 10°C/min heating rate. The thermal vacuum stability test involves the artificial aging of these materials at 100°C for 40 h and measuring the pressure inside the test tube. Chemical stability was reported as specific volume of gases released in this time interval. The tests were performed in agreement with STANAG 4556.

The humidity of the pyrotechnic compositions was measured by weighting the samples before and after heating them at 100 °C for 30 min. Hygroscopicity was measured by weighting the dried samples before and after maintaining them into a closed desiccator containing a saturated solution of KNO_3 for 12 hours at 20 ±2°C.

Results and discussions
Theoretical evaluation of the physical, chemical, thermodynamic characteristics and the pyrotechnic effect is an intermediate step in developing a pyrotechnic composition, before proceeding to its development and experimentation. The thermodynamic properties are based on the combustion reaction equation (1):
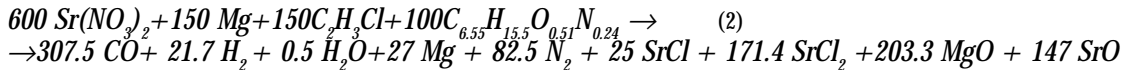
$$-R+P+Q_M^* \to 0 \qquad (1)$$

where: R = reactants, P = reaction products, Q_M^* = heat of combustion;

Table 2 illustrates the thermodynamic characteristics of the reactants and the reaction products. The theoretical studies allow the evaluation of the thermodynamic characteristics, such as heat of combustion and specific volume, which depend on the chemical composition of the reaction products. The mass form and the molar form of the combustion reaction equations of the pyrotechnic
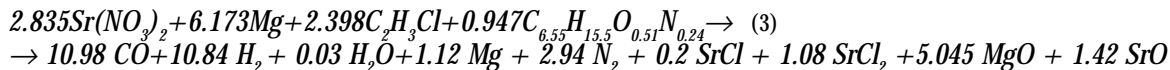
compositions, calculated with CEA software, are presented below:

PC-1 - red flame signaling composition
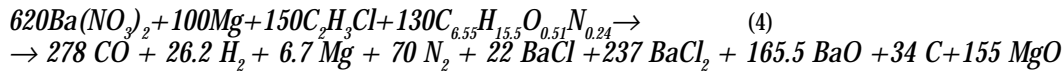Combustion reaction ecuation – mass form

$$600\ Sr(NO_3)_2 + 150\ Mg + 150C_2H_3Cl + 100C_{6.55}H_{15.5}O_{0.51}N_{0.24} \rightarrow \quad (2)$$
$$\rightarrow 307.5\ CO + 21.7\ H_2 + 0.5\ H_2O + 27\ Mg + 82.5\ N_2 + 25\ SrCl + 171.4\ SrCl_2 + 203.3\ MgO + 147\ SrO$$

Combustion reaction ecuation – molar form

$$2.835Sr(NO_3)_2 + 6.173Mg + 2.398C_2H_3Cl + 0.947C_{6.55}H_{15.5}O_{0.51}N_{0.24} \rightarrow \quad (3)$$
$$\rightarrow 10.98\ CO + 10.84\ H_2 + 0.03\ H_2O + 1.12\ Mg + 2.94\ N_2 + 0.2\ SrCl + 1.08\ SrCl_2 + 5.045\ MgO + 1.42\ SrO$$

PC-2 - green flame signaling composition
Combustion reaction ecuation – mass form

$$620Ba(NO_3)_2 + 100Mg + 150C_2H_3Cl + 130C_{6.55}H_{15.5}O_{0.51}N_{0.24} \rightarrow \quad (4)$$
$$\rightarrow 278\ CO + 26.2\ H_2 + 6.7\ Mg + 70\ N_2 + 22\ BaCl + 237\ BaCl_2 + 165.5\ BaO + 34\ C + 155\ MgO$$

Combustion reaction ecuation – molar form

$$2.372Ba(NO_3)_2 + 4.2Mg + 2,398C_2H_3Cl + 1.231C_{6.55}H_{15.5}O_{0.51}N_{0.24} \rightarrow \quad (5)$$
$$\rightarrow 9.94\ CO + 13.1\ H_2 + 0.27\ Mg + 2.5\ N_2 + 0.13\ BaCl + 1.13\ BaCl_2 + 1.08\ BaO + 2.9\ C + 3.84\ MgO$$
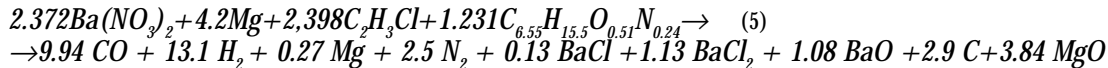
PC-3 - smoke generating pyrotechnic composition
Combustion reaction ecuation – mass form

$$660\ KNO_3 + 270P + 70C_{6.55}H_{15.5}O_{0.51}N_{0.24} \rightarrow \quad (6)$$
$$\rightarrow 57\ CO + 22.6\ CO_2 + 5.1\ H_2 + 29.8\ H_2O + 43.1\ K + 97.5\ KOH + 93.6\ N_2 + 88.1\ P_2 + 274.4\ P_2O_3 + 18.5\ P_4 + 246.2\ K_2CO_3$$

Combustion reaction ecuation – molar form

$$6,528\ KNO_3 + 8,709\ P + 0.045\ C_{6.55}H_{15.5}O_{0.51}N_{0.24} \rightarrow \quad (7)$$
$$\rightarrow 2.035\ CO + 0.514\ CO_2 + 2.55\ H_2 + 1.66\ H_2O + 1.1\ K + 1.7\ KOH + 3.34\ N_2 + 1.41\ P_2 + 2.494\ P_2O_3 + 0.15\ P_4 + 1.781\ K_2CO_3$$
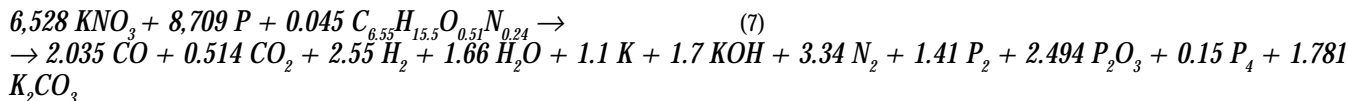
Table 2
THERMODYNAMIC CHARACTERISTICS

Material	M_i [g/mol]	$\Delta_f H^0$ [kcal/mol]	ρ [g/cm³]
Sr(NO₃)₂	211.63	230.9	2.986
Ba(NO₃)₂	261.38	234.6	3.24
KNO₃	101.1	116.93	2.109
Mg	24.3	0	1.74
RP	31	4.2	2.2
C₂H₃Cl	62.55	23.0	1.4
Binder	105.62	45.58	1.2

Table 3
THEORETICAL RESULTS

	PC-1	PC-2	PC-3
Combustion temperature $T_{Th.}$ [K]	2151.5	1825.1	1496.2
Specific volume $V_{0sp Th.}$ [l/kg]	555.5	572.0	322.5

The theoretical calculations results are indicated in table 3.

The heat of combustion and the specific volume are directly related to the pyrotechnic effect. These thermodynamic properties were experimentally measured and the results are shown in table 4 and table 5. These

Table 4
HEAT OF COMBUSTION AND SPECIFIC VOLUME

	Heat of combustion / Specific volume	Sample 1	Sample 2	Sample 3
PC-1	Q_v [kcal/kg]	988.7	979.6	989.5
	V_{0sp} [l/kg]	475.6	480.4	472.3
PC-2	Q_v [kcal/kg]	848.0	847.4	852.2
	V_{0sp} [l/kg]	485.4	480.0	490.0
PC-3	Q_v [kcal/kg]	925.7	921.5	921.7
	V_{0sp} [l/kg]	309.3	330.0	320.2

Average	PC-1	PC-2	PC-3	
Heat of combustion Q_{vExp} [kcal/kg]	985.9	849.2	923.0	**Table 5** AVERAGE VALUES FOR HEAT OF COMBUSTION AND SPECIFIC VOLUME
Theoretical specific volume $V_{0spTh.}$ [l/kg]	555,5	572.0	322.5	
Experimental specific volume $V_{0spExp.}$ [l/kg]	476.1	385.1	319.8	

values allow the evaluation of the theoretical model proposed for the combustion reaction equations.

Shidlovski [15] indicates that the heat of combustion should be superior to 800 kcal/kg and combustion temperatures ~ 2000 °C in order to volatilize and excite the emitter compounds and, thus, obtain optimal illuminating effects. The specific volumes are not extremely important for the colored flame and smoke compositions, but they can influence the evacuation in the environment of the solid products responsible for the main pyrotechnic effect and can also influence the burning propagation phenomena. Typically, pyrotechnic compositions have lower specific volumes (under 600 L/kg), when compared with high explosives, due to their high yield of solid products [3].

The experimental results are in good correlation with the theoretical calculations in respect to the specific volume. High combustion temperatures (close to 2000 °C) were calculated for PC-1 and PC-2, indicating good conditions for emission and excitation of active species (barium and strontium chlorides).

Loading density calculation is necessary for the evaluation of the mass flow and the interdependence with the burning rate. Loading density represents the ratio between the composition weight and the volume occupied. This value is lower than the theoretical value obtained by this equation:

$$\rho_{TMD} = \frac{1}{\sum \frac{p_i}{\rho_i}} \qquad (8)$$

where ρ_{TMD} is the theoretical maximum density; p_i and ρ_i are mass and volume ratios for a number of i components. For the calculation of the loading density, a small amount of pyrotechnic composition was manually pressed in a cylindrical mold (Φ = diameter, S = transversal area). After being pressed, the cylinders obtained were measured

and weighted. The results obtained for the three pyrotechnic compositions are illustrated in tables 6-8.

The burning rate depends on the chemical composition, loading density and confinement. The burning rate and the length of the pyrotechnic relay influence the combustion time and the pyrotechnic effect duration. In the case of a plastic pyrotechnic composition, burning rate is necessary for choosing the appropriate length of the pyrotechnic relay. The burning rate represents the ratio between the combustion height and the combustion time and the results of these measurements are shown in table 9. The combustion was stable and the burning rates were appropriate for the purpose needed.

Figure 1 ilustrates how these plastic pyrotechnic compositions can be modeled and shaped in different geometries.

The mechanical strength of the pyrotechnic compositions are influenced by multiple parameters: particle size and distribution, binder characteristics, processing method, loading density, pressing conditions, deformation strain rate, thermal history, storage and test temperature and relative humidity of storage environment [7].

The recorded stress-strain curves indicate that the two materials stop obeying Hooke's law already in the early region of the graph; the proportional limit can be considered below 2% strain. Young modulus was estimated at 0.5% strain, with an average value of 0.75 ± 0.08 MPa for PC-1

Fig. 1. Modeling a plastic pyrotechnic compositions

Sample	D [mm]	S [cm²]	H [mm]	V [cm³]	m [g]	ρ [g/cm³]	
1	10	0.785	16.1	1.264	1.55	1.226	
2	10	0.785	19.0	1.492	1.86	1.247	
3	10	0.785	19.4	1.523	1.89	1.241	**Table 6** PC-1 LOADING DENSITY
Average						*1.238*	
1	18.65	2.730	16.8	4.587	5.78	1.260	
2	18.65	2.730	15.2	4.150	5.12	1.234	
3	18.65	2.730	11.7	3.195	4.0	1.252	
Average						*1.249*	

Sample	D [mm]	S [cm²]	H [mm]	V [cm³]	m [g]	ρ [g/cm³]
1	10	0.785	8.41	0.660	0.89	1.348
2	10	0.785	12.32	0.967	1.35	1.396
3	10	0.785	11.53	0.905	1.23	1.359
Average						*1.368*
1	18.65	2.730	12.92	3.528	4.82	1.366
2	18.65	2.730	7.49	2.045	2.58	1.262
3	18.65	2.730	10.21	2.788	3.77	1.352
Average						*1.327*

Table 7
PC-2 LOADING DENSITY

Sample	D [mm]	S [cm²]	H [mm]	V [cm³]	m [g]	ρ [g/cm³]
1	10	0.785	10.7	0.840	1.2	1.429
2	10	0.785	4.2	0.330	0.46	1.395
3	10	0.785	5.2	0.408	0.59	1.445
Average						*1.423*
1	18.65	2.730	13	3.550	5	1.409
2	18.65	2.730	12.3	3.358	4.91	1.462
3	18.65	2.730	12.8	3.495	4.8	1.373
Average						*1.415*

Table 8
PC-3 LOADING DENSITY

	Property	Sample 1	Sample 2	Sample 3	Average
PC-1	u [mm/s]	1.34	1.69	1.57	*1.53*
	$\dot{m}$ [g/s]	0.130	0.168	0.154	*0.15*
PC-2	u [mm/s]	1.20	1.19	1.07	*1.15*
	$\dot{m}$ [g/s]	0.130	0.126	0.119	*0.12*
PC-3	u [mm/s]	1.06	1.61	1.68	*1.45*
	$\dot{m}$ [g/s]	0.118	0.180	0.184	*0.16*

Table 9
BURNING RATES OF THE PYROTECHNIC COMPOSITIONS

and 0.36± 0.04 MPa for PC-2 (fig. 2). As strain increases, a stress-induced *plastic* flow occurs in each specimen, stating for the capacity of the investigated specimens to undergo a rearrangement of their internal molecular or microscopic structure (fig. 3). Such behavior is characteristic for materials with structural mobility allowing new equilibrium positions with increasing strain. This confirms the plasticity of the investigated materials.

Moreover, although PC-1 samples have a higher elasticity modulus, and consequently being more rigid then PC-2 samples, the compression tests showed that they require a greater stress in order to reach the breaking point (inset in fig. 3). These findings confirm a more elastic behavior of PC-2 versus PC-1.

Fracture at the edges of the materials can be macroscopically noticed at strain values above 14% for PC-1 and 16% for PC-2.

The thermal behaviour of the pyrotechnic compositions, namely the self-ignition temperature (thermal sensitivity) and thermal vacuum stability, represents an important feature among the safety characteristics for this type of
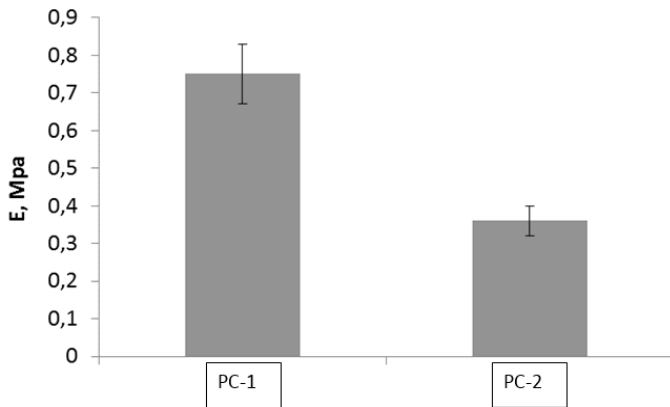
Fig. 2. Young modulus (E, MPa) estimated at 0.5% strain. Inset – stress-strain curves.
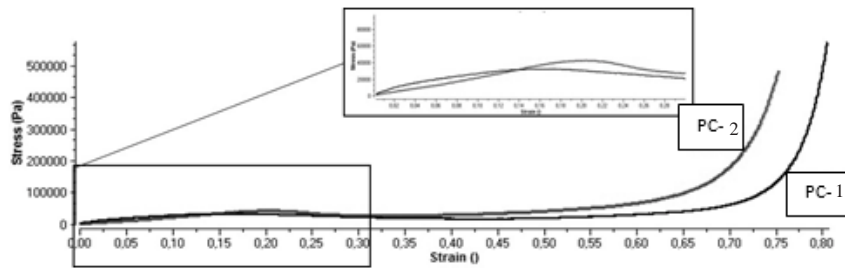

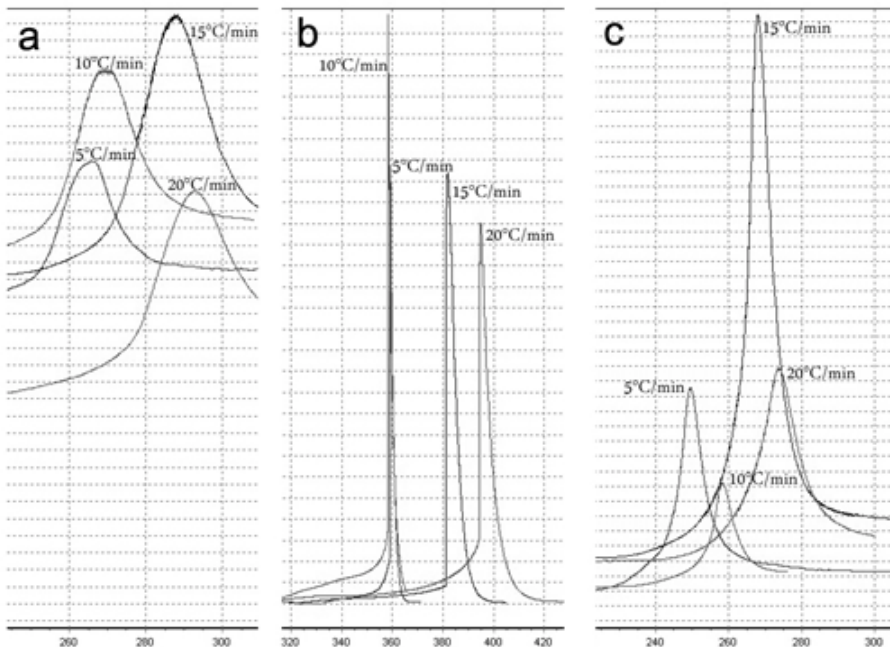Fig. 3. Strain-stress curves for PC-1 and PC-2

Fig. 4. DTA traces of the pyrotechnic compositions: (a) PC-1; (b) PC-2; (c) PC-3; Heating rates: 5°C/min, 10°C/min, 15°C/min, 20°C/min

materials. The temperatures (table 10) coresponding to the exothermic peaks illustrated in figure 4 can be assigned to the decomposition process generated by samples self-ignition. These temperatures depend on the heating rate, presenting higher values when the heating rate increases [16]. The values in table 10 indicate that all the compositions develop exothermic decomposition above 200 °C, therefore they present a low temperature sensitivity.

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The thermal stability of the pyrotehnic composition (table 11) was evaluated by measuring the volume of gaseous reaction products generated when the samples were maintained at 100°C for 40 h in order to stimulate yhe aging process of the material.The nergetic materials with a specific volume greater than 2 cm³ / g are considered to have reduced chemical stability, therefore these pyrotehnic composition can be considered chemically stable.

When pyrotechnic compositions are exposed to various storage conditions, the relative humidity and their moisture absorbing capacity can influence their performances. Values under 1% for these parameters are usually requested. The moisture content of the samples was calculated as follows:

$$x = \frac{m_1 - m_2}{m_1} \cdot 100 \qquad (9)$$

where m_1 represents the mass of the sample before drying [g] and m_2 is the mass of the sample after drying [g], and the results are illustrated in table 12.

	Sample	Heating rate [°C/min]	Beginning temp. [°C]	Onset temp. [°C]	Top temp. [°C]	Max. diff. [°C]
PC-1	1	5	242.52	252.52	266.10	4.46
	2	10	237.80	257.78	270.23	7.14
	3	15	232.09	271.17	288.51	8.76
	4	20	204.93	272.79	292.73	3.57
PC-2	1	5	212.46	243.76	249.48	13.53
	2	10	227.12	253.86	258.27	7.26
	3	15	227.39	262.78	268.03	38.47
	4	20	236.20	263.63	273.50	14.88
PC-3	1	5	342.37	359.12	359.19	207.39
	2	10	312.89	358.25	358.37	278.82
	3	15	322.63	380.84	381.74	203.90
	4	20	328.40	393.34	394.87	180.04

Table 10
THERMAL PROPERTIES OF THE PYROTECHNIC COMPOSITIONS

Composition	PC-1	PC-2	PC-3
V_{0SP} [cm^3/g]	0.183	0.19	1.71

Table 11
THERMAL VACUUM STABILITY OF THE PYROTECHNIC COMPOSITIONS

[%]	PC-1	PC-2	PC-3
humidity h_r / higroscopicity u_r	0.07/0.18	0.04/0.05	0.93/1.25

Table 12
HUMIDITY AND HIGROSCOPICITY OF THE PYROTECHNIC COMPOSITIONS

The dry samples were weighted before and after exposure to moisture and the values obtained for hygroscopicity are shown in the same table.

Conclusions

Three novel hand moldable plastic pyrotechnic compositions with colored flame or white smoke effects were developed. Mechanical characterization of the mixtures demonstrated they possess appropriate plasticity for manual packing in various geometrical shapes. Further, their performance characteristics were determined theoretically and experimentally. The values obtained for heat of combustion, temperature of combustion, specific volume and burning rates are in good agreement with those required for colored flame and smoke generating compositions. Further testing showed excellent chemical stability, low hygroscopicity and temperature sensitivity, indicating a good agreement with the general safety requirements for energetic materials.

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