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PHASE STABILIZED AMMONIUM NITRATE FOR FUTURE GREEN ROCKET PROPELLANTS

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In the context of high concerns related to the environmental risk posed by ammonium perchlorate (AP), the main oxidizer for rocket propellants, the investigation of alternative comburant species became one of the top priorities in the field of energetic materials. Ammonium nitrate (AN) could be a cheap and available oxidizer, but its polymorphic nature at ambient temperatures has limited its use in polymeric composite propellants.

In this study, we have investigated the effectiveness of stabilizing additives that would suppress phase transition of ammonium nitrate at ambient temperatures. This would minimize the risks associated with AN handling, transport, and storage, when used as an environmentally friendly oxidizer in composite solid propellants. Various potassium-based additives were used for co-crystallization of ammonium nitrate and changes in polymorphic transitions were evaluated. Furthermore, composite formulations based on PSAN and different polyurethanes were investigated in terms of safety and performance characteristics.

Keywords: ammonium nitrate; composite propellants; eco-friendly; polyurethanes; PSAN

1. Introduction

A green composite propellant or an environmentally friendly composite propellant (ECP) consists in a heterogeneous formulation, eco-oxidizer-metallic fuel-binder matrix, with improved performances (such as a high specific impulse) and a reduced environmental impact during operation.

From a functional and structural point of view, a solid rocket composite rocket propellant is a heterogeneous system that can sustain the combustion process without the atmospheric oxygen generating a high amount of hot gases at elevated

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pressure. Thus, the oxidizer is the vital ingredient of the propellant. Currently, ammonium perchlorate is the most reliable oxidizer for the solid composite propellants formulations in military and aerospace applications, due to its excellent performance characteristics (high oxygen balance, burning rate, specific impulse, density) and long-term stability in storage [1-3]. But in the green context, its established disadvantages (chlorinated compounds and perchlorates residues) [4,5], cannot be overlooked. These harmful combustion products have a negative impact on the environment (acid rain, ozone layer depletion, contamination of aquifer) [4,5] and on the personnel operating the launch system (thyroid-linked diseases) [6].

The investigation of alternative comburant species became one of the top priorities in the field of rocketry. Therefore, in order to be in tune with the environmental awareness and environmental directives green oxidizers such as ammonium nitrate (AN), ammonium dinitramide (ADN), hydroxyl ammonium nitrate (HAN) and hydrazinium nitroformate (HNF) are intensively studied [7-11].

Given the requirements trio: financial impact, safety, and performance, which must be considered when it comes to substitute one material with another, AN is the most suitable candidate, in the current context. AN, or NH_4NO_3, is a smokeless, chlorine free compound, with an insignificant impact to the environment. Due to its inferior energetic characteristics, hygroscopicity and polymorphic nature at ambient temperatures, its applicability is limited in polymeric composite propellants.

Although issues related to combustion rate and hygroscopicity could be overpassed by a metallic fuel [12,13], an energetic binder [14] and coating agents, to avoid ambient moisture [15], when it comes to the hazardous polymorphic nature at ambient temperatures, phase IV−III, it is a completely different subject. This phenomenon resumes to density/volume changes that affect the integrity and mechanical properties of the propellant grain [7,8,16]. The crystalline forms of AN as a temperature dependence are the following: -17℃ (V ↔ IV); +32℃ (IV ↔ III); +84℃ (III ↔ II); +125℃ (II ↔ I); +169℃) [17].

Despite this fact, specialized studies have shown there are several solutions in this area. The phase IV-III transition can be suppressed by various organic or inorganic compounds (polyvinyl pyrrolidine, polyethylene oxide, polyacrylamide, potassium salts and alkali metals). The co-crystallization product is known in the specific literature as phase stabilized ammonium nitrate, or PSAN. [7,8,16,17].

The novelty of this study consists in the development of an eco-friendly composite propellant formulation, using the PSAN oxidizer and a metallic fuel, usually aluminum [12,13], which are mixed thoroughly, at a physical level, and encapsulated in a binder matrix (obtained usually from a liquid pre-polymer and a cross-linking agent, with a specific viscosity to allow casting) which, in addition to the aforementioned purpose, also serves as organic fuel.

The polymeric binder's nature directly influences the ballistics of the propellant's, but also gives the mechanical features of the composite material. A perfect binder should possess a low Tg (glass transition temperature), good traction/compression strength, good shock resistance, and a long shelf life [18, 19].

This study investigates the effectiveness of various potassium-based additives, potassium nitrate (KNO_3), potassium chromate (K_2CrO_4), potassium dichromate ($K_2Cr_2O_7$), potassium sulfate (K_2SO_4), potassium chlorate ($KClO_3$), potassium perchlorate ($KClO_4$), used for co-crystallization of AN, in the suppressing process of the phase transition at ambient temperatures. Furthermore, eco-friendly polymeric composite formulations based on PSAN and different polyurethanes were investigated in terms of safety and performance characteristics.

2. Experimental section

2.1. Materials

Ammonium nitrate (AN, Sigma Aldrich), potassium nitrate (KN, Sigma Aldrich), potassium chromate (KCr, Sigma Aldrich), Potassium dichromate (KDCr, Sigma Aldrich), potassium sulfate (KS, Sigma Aldrich), potassium chlorate (KCl, Sigma Aldrich), potassium perchlorate (KPCl, Sigma Aldrich), diphenylmethane-4,4′-diisocyanate (MDI, technical product Desmodur® R 44V20L, Bayer), isophorone diisocyanate (IPDI, Sigma Alridch), Sethatane D 1160 (Nuplex), aluminum (Al, dark pyro, PyroGarage), were used as received. Triethylene glycol dinitrate (TEGDN), an energetic plasticizer, was synthesized at MTA according to literature data [20]. Polyols from recycled PET (PR-PET) were synthesized by degradation of PET with ethylene glycol by a specialized laboratory from National Institute for Research and Development for Chemistry and Petrochemistry (INCDCP - ICECHIM).

2.2 Methods

PSAN synthesis

A concentrated solution was prepared by dissolving 90 g AN in 200 mL of aqueous solution (distillated water) at 25℃. The solution was gently stirred (50rpm) for 45 min. After complete dissolution of AN, 10 g of K-based additive were added to the solution which was stirred until complete solubilization. The dissolving process was followed by co-crystallization in a ventilated drying oven at 50℃ for 72 h. After 72 hours, the mixture obtained was collected and stored in a desiccator to avoid environmental moisture. In table 1, are presented PSAN formulations with various K-based additives.

Table 1

PSAN formulations with various K-based additives

PSAN Compound	PSAN_0	PSAN_1	PSAN_6	PSAN_15	PSAN_16	PSAN_17
NH_4NO_3	✓	✓	✓	✓	✓	✓
KNO_3	✓					
K_2CrO_4		✓				
$K_2Cr_2O_7$			✓			
$KClO_3$				✓		
K_2SO_4					✓	
$KClO_4$						✓

ECP preparation

Given the heterogeneous structure of an ECP: environmentally friendly oxidizer, metallic fuel and binder matrix, the preparation procedure was performed through the following simultaneous working directions:

The first step consisted in the synthesis of the binder matrix, polyurethane-plasticizer, as follows: initially, the mixture of polyols was prepared, over which isocyanate was added, except for the binders which included the other energetic plasticizer, TEGDN, added prior isocyanate. The diisocyanates involved in the crosslinking of the polyurethane binder were IPDI, an aliphatic diisocyanate and MDI, an aromatic diisocyanate. The two components (polyols and isocyanates) were mixed in a ratio of 1:1. The Second step consisted in obtaining the solid mixture of PSAN and Al pyro dark. PSAN particles were sieved and the size used further into the propellant formulations was 200-300µm. The ingredients were mixed until complete homogenization, followed by wet pressing in 3D printed molds. Table 2 shows the composition of the ECP formulations.

Table 2

ECP formulations

Propellant acronym	Compound proportion [%]					
	Binder matrix				PSAN	Al Dark
	BM-9	BM-10	BM-11	BM-12		
ECP-9	20				70	10
ECP-10		20			70	10
ECP-11			20		70	10
ECP-12				20	70	10

2.3. Characterization

Polymorphic behavior of PSAN was studied by thermal analysis with a differential scanning calorimeter (Perkin Elmer Diamond DSC apparatus) and a differential thermal analyzer (OZM 551-Ex apparatus). In case of DSC analysis, 5 mg of the sample was heated from -30℃ to 240℃ under nitrogen flow, while DTA analysis were performed using 40 mg samples heated from 20℃ to 250℃ in air. The heating rate in both cases was 5℃/min.

The FT-IR spectra of the synthesized PSAN were recorded using a Bruker VERTEX 70 Spectrometer with ATR. The parameters used for the determination of each spectrum were as follows: number of scans: 32; resolution: 4 cm^{-1}; spectral range: 700−4000 cm^{-1}. Approximately 4 mg of the PSAN specimen was used in each test.

To assess the safety and performance characteristics of the ECP formulations, several tests were performed, as follows:

- Friction sensitivity was determined using a BAM friction apparatus; 30 trials were performed for each sample with the maximum loading force of 360 N.
- Dynamic mechanical properties were determined using a DMA (dynamic mechanical analysis) TRITEC 2000 B apparatus. The specimens with dimensions of 10 mm × 9 mm × 3 mm, were analyzed in a single cantilever bending mode, between –50°C and +100°C, using a heating rate of 5℃/ min.
- Combustion heat and specific volume were determined for 2g sample with an adiabatic calorimeter AVL and a Julius-Peters gas-meter. 2 tests were carried out for each composite, under vacuum condition.
- Vacuum stability tests (VST) were conducted according to STANAG 4556-2A with a STABIL apparatus, where 5 g of sample were heated at 100°C for 40 hours under vacuum and the released volume gas was recorded by a pressure transducer connected to a computer.

3. Results and discussion

3.1. PSAN polymorphic characterization

Thermal analysis of unstabilized AN showed five endothermic transformations, the first four can be associated with crystalline transitions, while the last corresponds to the solid-liquid transition.

The analysis of PSAN specimens by DTA and DSC, showed that the phase transition at ambient temperature disappears in most cases, PSAN_0, PSAN_1, PSAN_15, PSAN_16 and PSAN_17. It should be noted that in the case of PSAN_6 it does not happen, and it behaves as AN.

The third phase takes place over 100℃, while the second and first transformation differs depending on the case. Transition to phase II, for PSAN_0, PSAN_1, PSAN_17 appears around 120℃, similar with AN, while for PSAN_15, PSAN_16 much later around 140℃. The starting temperature for phase I varies a lot, PSAN_0, like AN, PSAN_1 and PSAN_6 around 135℃, PSAN_15, PSAN_16 around 165℃, close to the AN solid to liquid transition.

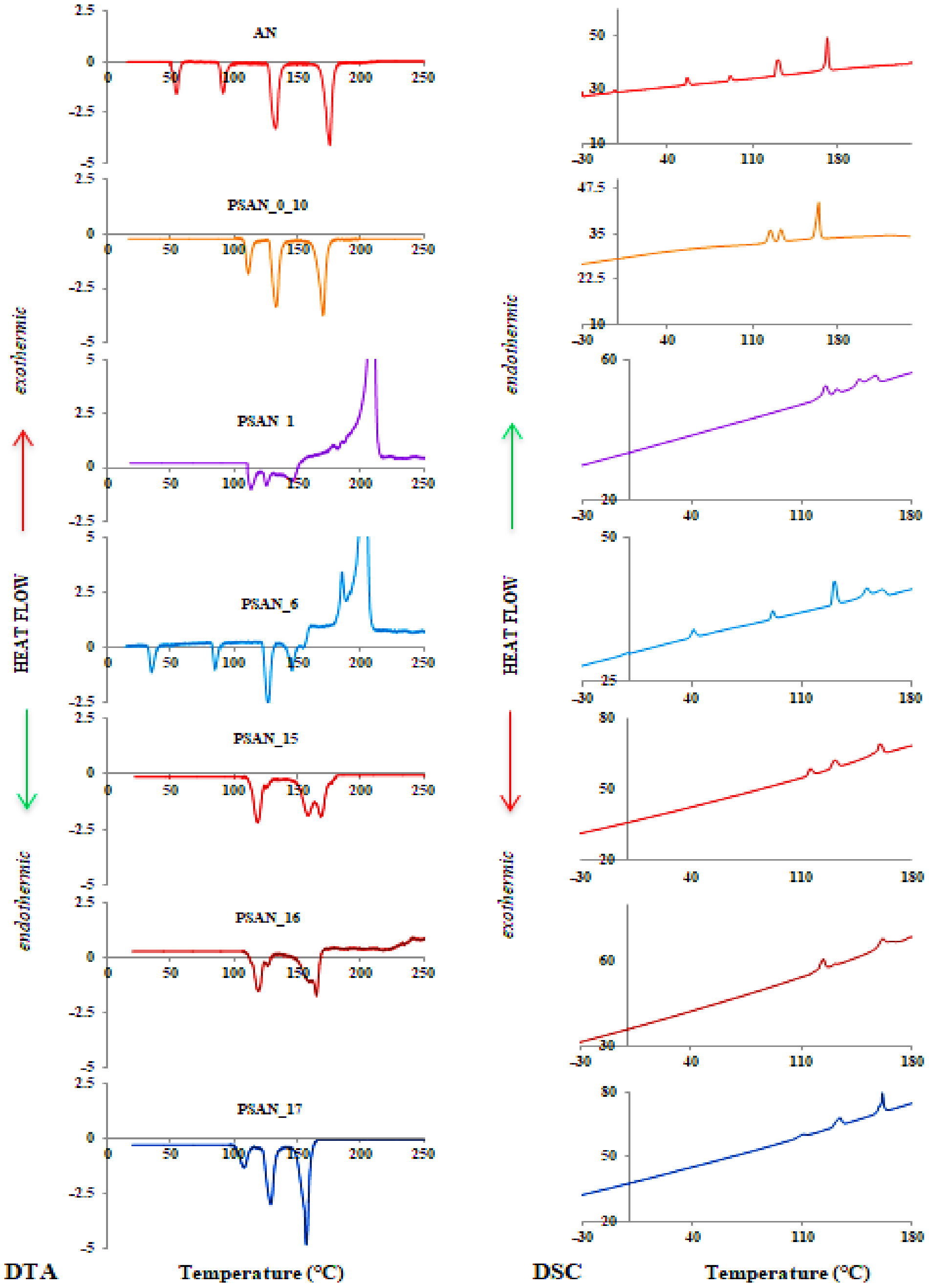

Fig. 1. DTA and DSC curves of AN and PSAN specimens

Another aspect that can only be distinguished in the PSAN_1 and PSAN_6 is the exothermic peak, around 170℃, which corresponds to an exothermal decomposition.

The DTA and DSC thermograms are depicted in Fig. 1 and Table 3.

Table 3

DTA and DSC results for PSAN specimens

Peak PSAN		P1			P2			P3			P4		
		Start	Onset	Top	Start	Onset	Top	Start	Onset	Top	Start	Onset	Top
AN [°C]	DTA	42	51	54	85	88	91	125	126	132	159	169	175
	DSC	38	39	42	89	91	93	128	129	132	168	171	172
PSAN_0 [°C]	DTA	-	-	-	104	107	111	125	127	133	155	164	170
	DSC	-	-	-	115	121	124	126	130	133	157	161	164
PSAN_1 [°C]	DTA	-	-	-	101	109	113	121	122	125	137	139	145
	DSC	-	-	-	119	123	125	129	131	133	142	144	147
PSAN_6 [°C]	DTA	29	31	35	80	82	85	120	122	126	134	140	145
	DSC	37	39	41	87	89	92	128	129	131	147	149	151
PSAN_15 [°C]	DTA	-	-	-	108	112	118	142	152	158	163	165	168
	DSC	-	-	-	110	113	115	126	128	131	157	158	160
PSAN_16 [°C]	DTA	-	-	-	106	113	119	140	149	159	161	162	165
	DSC	-	-	-	118	120	123	128	130	133	155	158	161
PSAN_17 [°C]	DTA	-	-	-	97	100	107	119	122	128	142	153	157
	DSC	-	-	-	105	107	110	127	129	133	155	158	160

Considering the requirements imposed by environmental legislation the compounds which possess in their structure harmful agents like chlorates, bichromates, perchlorates, chromates etc., are becoming more and more difficult to use. In this context, we decided to focus on a study on the optimization of the amount of potassium nitrate that can be used in the phase transition stabilization.

Different percentages of potassium nitrate, 0.1%, 1%, 2.5%, 5% and 6.5%, were added in order to optimize the amount of additive used in the stabilization. Following the DTA analyzes performed, it was observed that once the amount of additive is reduced, the endothermic transformation representative for phase III occurs earlier. This is shown in Fig. 2 and the values obtained for each PSAN_0 are depicted in Table 4.

Table 4

DTA results for various PSAN_0 specimens

PSAN Peak		PSAN_0_0.1 [°C]	PSAN_0_1 [°C]	PSAN_0_2.5 [°C]	PSAN_0_5 [°C]	PSAN_0_6.5 [°C]
P1	Start	40.95	-	-	-	-
	Onset	19.31	-	-	-	-
	Top	50.80	-	-	-	-
P2	Start	86.51	89.99	89.03	98.33	102.63
	Onset	88.31	91.79	91.39	100.58	105.06
	Top	92.29	94.35	96.92	105.05	108.80
P3	Start	125.01	121.54	120.41	120.76	121.78
	Onset	127.98	123.12	123.61	122.77	122.70
	Top	131.61	128.04	128.44	127.22	126.78
P4	Start	159.29	159.56	157.40	151.83	150.96
	Onset	167.54	163.36	162.01	158.43	154.49
	Top	173.46	169.17	167.78	165.21	162.86

Based on this analysis, it can be concluded that the optimal percentage of additive for AN stabilization, in the range 0 - 100 °C, is 5%, and the minimum amount leading to the disappearance of the phase transition at ambient temperatures is 1% (see Fig. 3). DSC results indicated the same behaviors as those of obtained from DTA tests.

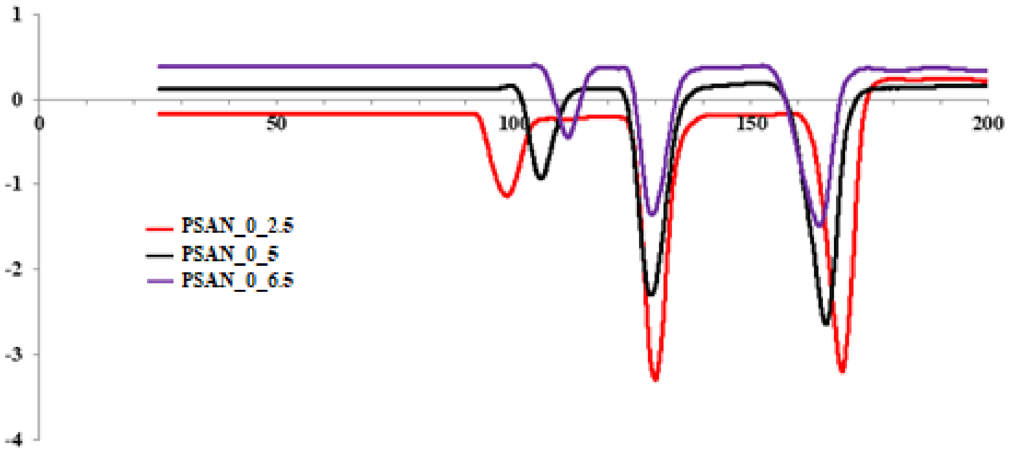

Fig. 2. DTA curves of PSAN_0_2.5, PSAN_0_5 and PSAN_0_6.5

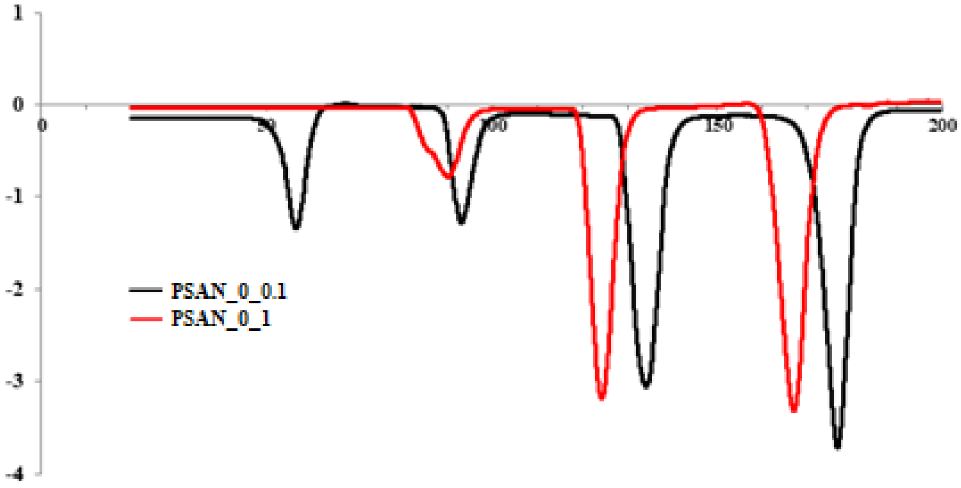

Fig. 3. DTA curves of PSAN_0_1 and PSAN_0_0.1

FT-IR analysis offered evidence of the components structure and the interactions established between them in PSAN mixtures.

The two peaks situated in 3300-2800 cm^{-1} interval can be attributed to the stretching vibrations associated to NH_4^+ while the peaks located in 2500-2300 can be assigned to NO_3^- stretching vibrations. The main spectral difference between AN phases can be observed in the intervals 1600–2800 cm$^{−1}$ and 650–1200 cm$^{−1}$. In the range of 1600–2800 cm$^{−1}$ AN possesses five specific absorption peaks. The intensity of all these peaks is attenuated in PSAN mixtures. Also, some peaks are slightly shifted indicating the interaction between PSAN components or a phase shift of the AN. In the region of 650–1200 cm$^{−1}$, there are three distinct visible peaks from NO_3^- stretching vibrations at 1041, 826, 714 cm$^{−1}$. Peaks located between 1600 and 1200 cm$^{−1}$ are usually attributed to NO_2 asymmetric stretch while the peaks in 900-650 cm$^{−1}$ range appear probably due to NH_2 wagging and asymmetric stretch.

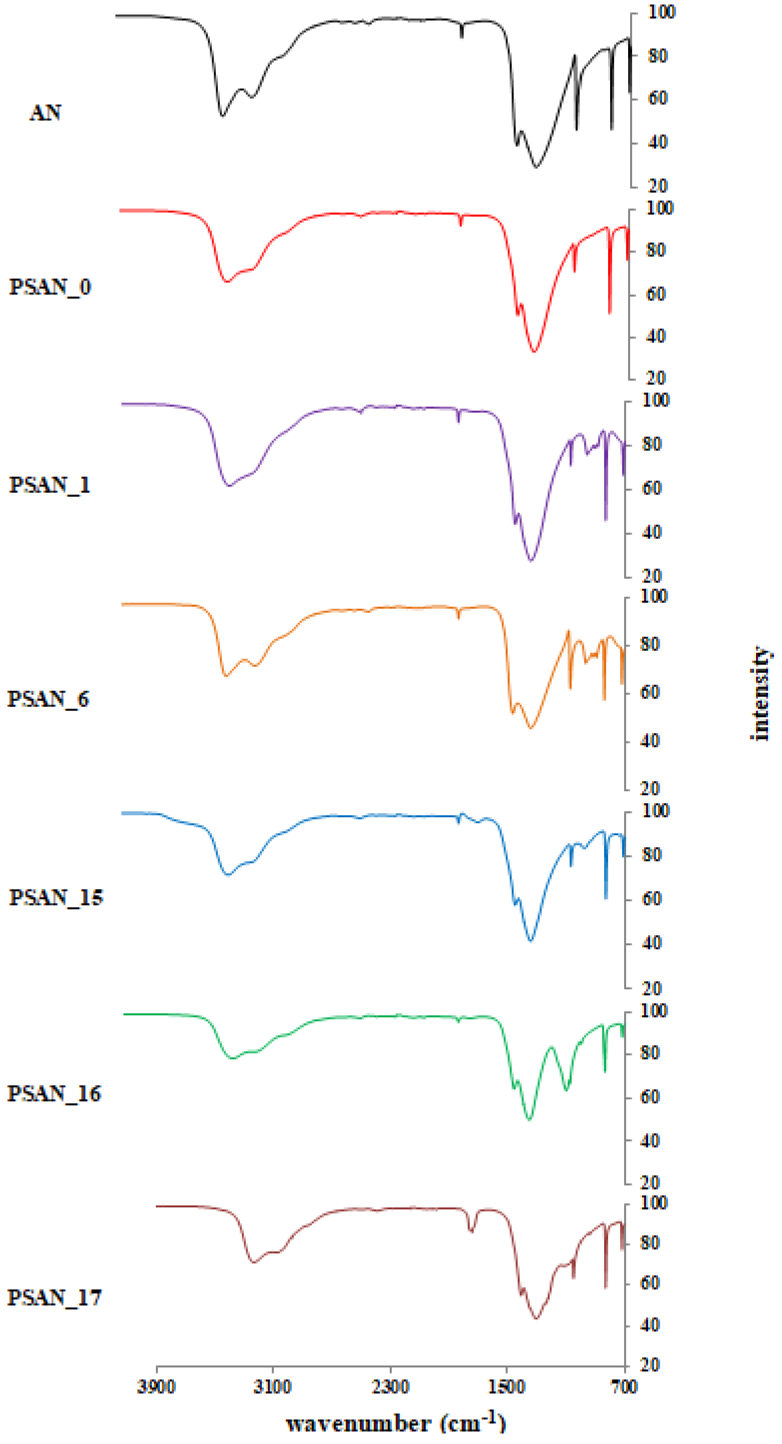

Fig. 4. IR curves of PSAN specimens

3.2. ECP characterization

The characterization of ECPs using DTA showed that all samples are stable up to about 170°C. Another aspect revealed is that polymeric composite formulations undergo the same three endothermic transformations that correspond to the PSAN phase transition. Thus, the presence of PSAN polymorphic transformations can be observed for each polymeric composite formulation at 112°C, 122°C and 142°C (see Fig. 5).

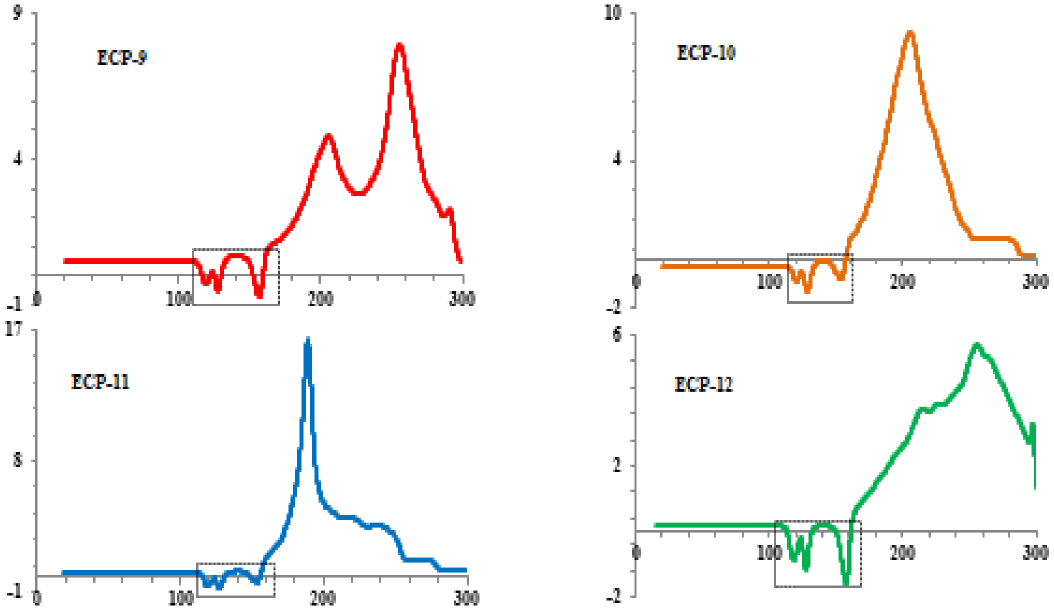

Fig. 5. DTA curves of ECP-9, ECP-10, ECP-11 and ECP-12

Friction sensitivity

In terms of safety, based on friction analysis results, it can be concluded that these types of polymeric composite propellants are completely insensitive to the mechanical friction stimulus.

Mechanical analysis

Dynamic Mechanical properties of ECP formulations, such as storage modulus (E′), loss modulus (E′′) and tan(δ), are reported as a temperature dependence. The DMA results for 1 Hz deformation frequency are depicted in Fig. 6.

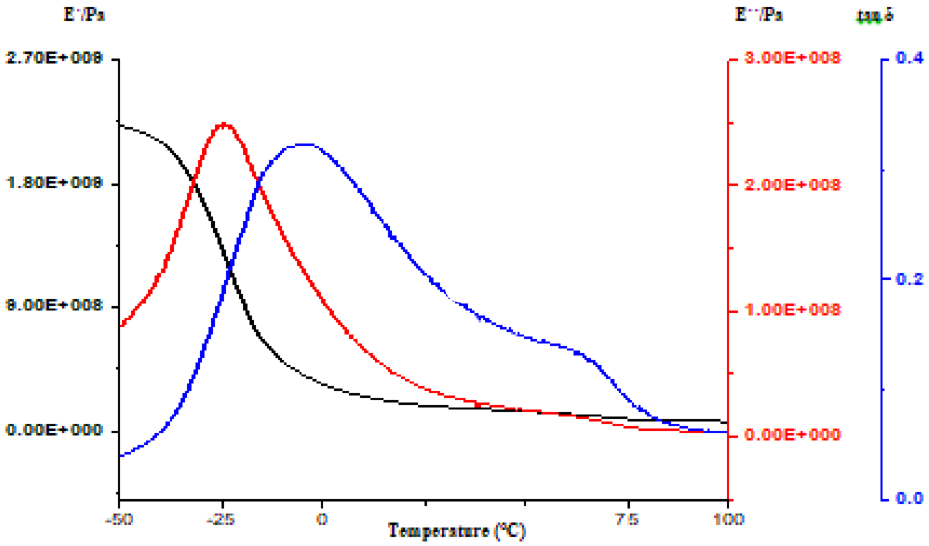

Fig. 6. ECPs storage modulus, loss modulus and tan (δ) versus temperature at 1 Hz

All the samples analyzed through DMA technique displayed similar behaviors, thus Fig. 6 is representative for all the samples tested. E' reflects the elastic stiffness of the material while E" is attributed to the energy loss of the sample. According to STANAG 4540 agreement [23], the maximum value of loss modulus E″ peak can be attributed to the corresponding temperature of Tg transition. The results for each ECP formulations are presented in Table 5. It must be noted that the value of the glass transition temperature is directly influenced by the chemical nature of the binder and in the case of solid composite propellants by the amount of the binder matrix.

Table 5

T_g Values for ECP formulations

ECPs Characteristic	ECP-9	ECP-10	ECP-11	ECP-12
T_g (°C)	-25.06	-23.72	-24.12	-24.83

Heat of combustion and specific volume

Heat of combustion is one of the main performance features of propellants. High heat of combustion gives high temperature of combustion products and subsequently higher pressure. From table 6 it can be noted that the caloric output of these PSAN based composite propellants is lower compared with typical AP compositions but is similar with those of double base propellants (nitrocellulose gels with nitroglycerine).

In the same time the gas output (specific volume) is much higher for PSAN based propellants and we are confident this could partly compensate the lower combustion heat.

Table 6

Average values for combustion heat and specific volume

ECPs / Characteristic	ECP-9	ECP-10	ECP-11	ECP-12	AP - based SRP (MAGIC)
Q_v [kcal/kg]	1032.41	982.96	1031.04	1050.32	1769.96
V_{sp} [l/kg]	712.23	690.25	700.27	718.46	557.43

Stability

Vacuum stability test is very important when providing data on the thermal stability of energetic formulations. During our tests the new PSAN based propellants released low quantity of gaseous products, exhibiting good thermal stability: while ECP-9 has a specific volume of 1.202 cm^3/g, ECP -10, ECP-11 and ECP-12 have 0.876 cm^3/g, 0.995 cm^3/g and 0.926 cm^3/g specific volumes.

4. Conclusions

In this study the effects of potassium salts in the tackling of AN phase transitions were investigated. The results observed were more than satisfactory. In the temperature range of -30 to +90℃, no endothermic peak was observed for stabilized AN. This means that the phase IV-III transition was eliminated, and phase III-II transition was shifted up, over 100℃. So, it seems that potassium salts are very effective on improving the polymorphic behavior of AN in the environmental temperature range. On the other hand, the performance and safety characteristics of composite formulations based on PSAN indicate that stabilized AN can be a suitable candidate oxidizer for future green rocket propellants.

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