The Contribution of the Polymeric Binder to the Improvement of the Mechanical Properties of Pyrotechnic Materials

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***Abstract*—This paper describes methods for investigating flare-type pyrotechnic compositions in order to determine the evolution over time of their mechanical properties directly influenced by the polymeric binder contained in the formulation. The role of antioxidants in the performance of the chosen polymeric binder is also investigated. For this, pyrotechnic compositions were prepared and tested, which were exposed to natural and accelerated aging.**

***Index Terms*—polyurethane, flare, mechanical properties, aging, antioxidant.**

I. Introduction

As it is known, energetic materials, and implicitly the pyrotechnic ones, are sensitive to heat and mechanical shocks, which can lead to the appearance of hot spots that cause detonation reactions [1]. Therefore, mechanical strength is one of the essential attributes of these materials, including those that are part of the pyrotechnic systems of the type of thermal countermeasures (flare), aerial countermeasures developed in order to deter missiles with IR guidance.

A typical formulation of pyrotechnic material includes as a basic element the binder, which has the role of maintaining the homogeneity of the composition, to cover and protect the particles of the component materials, but also to give it mechanical strength. The binders are selected according to the use of the pyrotechnic material and can be: natural binders (waxes, rosin, boiled linseed oil, shellac, etc.), which achieve good cohesion between particles, but do not give special mechanical properties, and synthetic binders (condensation products of phenol with formaldehyde, polyester, epoxy, polyamide, polyurethane, polyvinyl chloride and polyvinyl chloride resins, chlorinated rubber, thiocolic, etc.), which help to obtain pyrotechnic materials with high resistance to mechanical stress [2-5].

Polyurethane binders have become a staple in energetic compositions because they have the ability to create extremely durable polymer chains at low amounts of the compound in the formulation, thereby influencing only to a small extent the energetic capabilities of the composition. Other advantages of polyurethane binders are the lack of toxicity (solvent free), the ease of obtaining grains by squeeze casting, the high resistance to moisture and thermal shocks or other destructive factors that could affect the integrity of the ammunition [6, 7].

Most formulations of energy composites contain, in addition to the polymeric binder, also the antioxidant agent, with the role of protecting organic substances against oxidative degradation [8-10].

In this context, we aimed to investigate the influence of polymeric binder on the mechanical properties of some pyrotechnic compositions used to obtain flare-type ammunition, as well as the influence of antioxidant agents used in formulations on the chosen binder. For this, flare-type pyrotechnic compositions with and without antioxidant agent were prepared, exposed to natural and accelerated aging conditions and tested to monitor the evolution of mechanical properties and activity of the antioxidant agent over time.

II. Materials and Methods

A. Used Materials

For the formulation of flare pyrotechnic compositions a polyurethane binder was used consisting of a solvent free polyol based on castor oil, Setathane D 1160 (purity > 99.5%), NUPLEX supplier, solvent-free diphenylamino-diisocyanate, Suprasec 2496 (purity > 99%); magnesium powder (98% purity, 40 µm particle size), Pyrogarage supplier; aluminum powder (98% purity, 2 µm particle size), Pyrogarage supplier; chlorinated rubber, Parlon (99% purity, 5 µm particle size), Pyrogarage supplier, potassium perchlorate (98.5% purity, 88 µm particle size), Pyrogarage supplier; antioxidant agent, dibutyl-phenol (BHT - dibutylhydroxytoluene) (99% purity), Chemical supplier dissolved in acetone (99% purity), Chemical supplier, both forming a 20% solution. Methanol (99% purity), Chemical supplier, was also used for testing.

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B. Preparation Method

The potassium perchlorate was dried at 80°C for 24 hours and then sieved through a 74 µm sieve. The compositions were prepared by mixing metal powders with chlorinated rubber, over which potassium perchlorate was added and mixed gently. The polyurethane binder was prepared by mixing the polyol with the polyisocyanate up to 15 minutes before addition. The BHT solution dissolved in acetone was prepared separately. BHT solution and polyurethane binder were added to one half of the powder mixture, and only polyurethane binder was added to the other half. Homogeneous mixtures are obtained which are kept in metal molds for 24 hours.

In order to perform the mechanical tests, respectively the uniaxial tensile testing of the flare type pyrotechnic composition, samples of the shape and dimensions from Fig. 1 were cut from the blocks obtained in the way shown above.

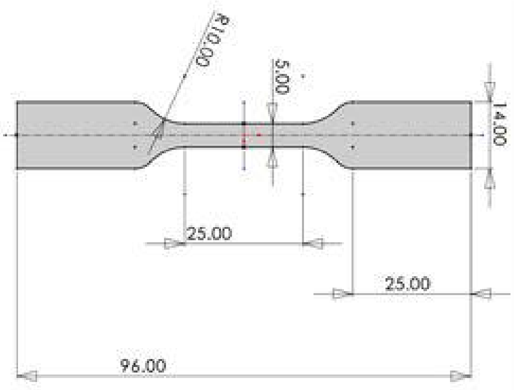

Figure 1. Shape and dimensions of uniaxial tensile strength test specimens

The test specimens were carefully cut on flat surfaces to prevent damage.

The preparation and storage of the samples was carried out in a controlled environment in terms of ambient temperature and humidity. The samples, both with antioxidant and without antioxidant, were protected against light and moisture by wrapping in aluminum foil. For testing, they were conditioned as follows: one part was exposed to natural aging by maintaining it at room temperature for 3 to 6 months, and the other part was artificially aged by holding at 60°C for 3 to 6 months. Artificial aging temperature and test times were predetermined to simulate the behavior of the ammunition during use [7].

To determine the antioxidant content, samples were taken from each composition, methanol was introduced for extraction and subjected to an ultrasound process for 4 hours. They were then filtered and kept in airtight glass containers for analysis.

C. Testing Methods

The tests were performed in three stages: after 7 days of the preparation of the composition (initial testing), after 3 months of natural and artificial aging, respectively, and after 6 months of also being aged naturally and artificially.

Mechanical properties testing is performed according to STANAG 4506 (Explosive materials. Physical/mechanical properties uniaxial tensile test). The samples were conditioned before testing for 12 hours at a temperature of 23 ± 5°C and a humidity of less than 30%. The tests were performed using a James Heall dynamometer, model TITAN 710, capable of maintaining a uniform force rate with the help of a servo-hydraulic system. The device is equipped with a load monitoring system, connected to the two clamps, fixed (lower) and mobile (upper), which records the force exerted on the test sample.

To attach the samples between the clamps of the device, a clamping adapter was designed (Fig. 2), which is fixed in the central position.

Figure 2. James Heall dynamometer and mounting adapter

The parameters established before the uniaxial tension test were: minimum distance between clamps 180 mm, elongation force max. 50 N and rate10 mm/min.

Five tests were performed for each sample, the test stopping at the time of irreversible deformation of the samples. The breaking force, *F* (N) and elongation (mm) were determined until the breaking point.

Quantitative determination of antioxidant content was performed by high performance liquid chromatography (HPLC), using the external standard method, based on the reference compound 2,6-di-tert-butyl-p-cresol, according to SMT 40651 - 2006 (Materials Composite fuels containing an inert binder (Assessment of aging characteristics)). The equipment used was the HPLC Finnigan Surveyor Plus, Thermo Scientific, with quadrupole pump - LC Pump Plus, UV-Vis diode array detector - PDA Plus Refractive index detector and detector and autosampler - Autosampler Plus, capillary column: Hypersil Green PAH 150 mm × 4.6 mm × 5 µm.

The operational parameters were: PDA PLUS detector; wavelength 280 nm; operating pressure 120 bar; mobile phase acetonitrile: water = 80:20, isocratic; mobile phase flow rate 3 ml/min.; injection volume 1 µl; autosampler temperature 30°C; column temperature 30°C.

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First, the calibration curve for the BHT quantification in the pyrotechnic composition was drawn, then the samples were analyzed, obtaining the concentration of the antioxidant agent.

III. Results and Discussion

Energetic binders are usually low molecular weight polymers with terminal hydroxyl groups and capable nitro or azido groups, which, together with the fuel and oxidant in the formulation, develop combustion reactions [10]. In this case, the binder consists of the polyurethane component (polyol polyester crosslinked with aromatic polyisocyanate), capable of giving very good mechanical and protective properties, but with lower energy properties, which are, however, offset by chlorinated rubber (chlorinated polyolefin) 65%). Energy compositions based on RDX combined with thermoplastic elastomers are already well known, such as: vinyl acetate-ethylene (EVA), butadiene-styrene or isoprene copolymers, polyurethanes and polybutylene-terephthalate / polyether-glycyl copolymers [11-13].

Theoretically, the presence of an antioxidant agent in a formulation attenuates the effects over time of environmental destructive factors: temperature, UV radiation, humidity, etc. Dibutyl-phenol is a lyophilic organic compound often used to prevent oxidation by free radicals, which also has low toxicity compared to other compounds in the same category. From a chemical point of view, BHT undergoes an oxidation process in the presence of atmospheric oxygen, UV radiation, humidity, preventing the formation of peroxides along the carbon chains containing double bonds of the binders and, implicitly, their breaking point [14].

In order to verify the influence of the binder on the mechanical properties of the pyrotechnic composition, the resistance to uniaxial tension of the samples was tested 7 days after preparation of the composition, after 3 months of exposure to natural and artificial aging, and after 6 months. In order to verify if the presence of BHT in the composition is improving the mechanical strength (by protecting the carbon catenary chains), samples of pyrotechnic composition with and without antioxidant agent exposed to natural and artificial aging were tested.

Table I. Tensile Strength 7 Days after Preparation

Sample No	Force (N)	Mean force (N)	Elongation (mm)	Mean Elongation (mm)
without antioxidant				
1	3.8		2.31	
2	4.53		2.81	
3	4.61	3.96	2.62	2.24
4	3.98		1.69	
5	2.89		1.78	
with antioxidant				
6	3.78		2.57	
7	4.53		1.69	
8	3.85	3.63	2.52	2.27
9	2.98		1.68	
10	3.03		2.92	

According to the data in Table I, it is observed that, initially, the pyrotechnic compositions have approximately the same mechanical properties, respectively, at a force of 3.5 – 4 N, a deformation of 2.2 mm is obtained until breaking.

After three months of natural aging, the tensile strength of the pyrotechnic compositions improves. For the same elongation a tensile force double in value is required. The presence of the oxidant does not significantly affect the mechanical properties of the composition.

Table II. Tensile Strength 3 Months after Preparation, Naturally Aged Material

Sample No.	Force (N)	Mean force (N)	Elongation (mm)	Mean elongation (mm)
without antioxidant				
1	7.79		2.34	
2	8.08		2.62	
3	10.74		2.99	
4	9.29	8.39	2.06	2.39
5	6.04		1.96	
with antioxidant				
6	6.28		2.06	
7	8.88		3.13	
8	6.53		2.4	
9	5.22	6.8	2.14	2.38
10	7.11		2.15	

After six months of natural aging, the mechanical strength of the pyrotechnic composition has improved considerably, requiring a force three times greater than the initial one to obtain an irreversible deformation of the test specimens.

Table III. Tensile Strength 6 Months after Preparation, Naturally Aged Material

Sample No.	Force (N)	Mean force (N)	Elongation (mm)	Mean elongation (mm)
without antioxidant				
1	16.93		3.75	
2	12.22		2.72	
3	19.2		3.46	
4	11.29	13.96	1.03	2.9
5	10.17		3.56	
with antioxidant				
6	9.96		2.06	
7	8.28		2.03	
8	10.44		3.4	
9	9.94	9.98	2.06	2.42
10	11.28		2.53	

In the case of accelerated aging, by exposing the test samples to 60°C, Tables IV and V show that the mechanical strength of the pyrotechnic compositions has increased compared to those naturally aged.

Table IV. Tensile Strength 3 Months after Preparation, Material Aged at $60^{O}C$

Sample No	Force (N)	Mean force (N)	Elongation (mm)	Mean elongation (mm)
without antioxidant				
1	16.17		1.87	
2	14.02		3.84	
3	16.08		2.34	
4	15.08	14.95	2.34	2.54
5	13.42		2.34	
with antioxidant				
6	12.08		2.06	
7	14.33		2.72	
8	11.93		2.43	2.32
9	13.07	13.33	2.25	
10	15.26		2.15	

TABLE V. TENSILE STRENGTH 6 MONTHS AFTER PREPARATION, MATERIAL AGED AT 60°C

Sample No.	Force (N)	Mean force (N)	Elongation (mm)	Mean elongation (mm)
without antioxidant				
1	16.64	18.24	2.81	2.9
2	16.03		2.04	
3	19.03		5.06	
4	20.57		2.34	
5	18.92		2.25	
with antioxidant				
6	15.15	16.89	2.31	2.37
7	17.55		2.25	
8	19.78		2.53	
9	16.46		2.4	
10	15.53		2.35	

The evolution over time of tensile strength for naturally and accelerated aging samples can also be seen in Fig. 3.

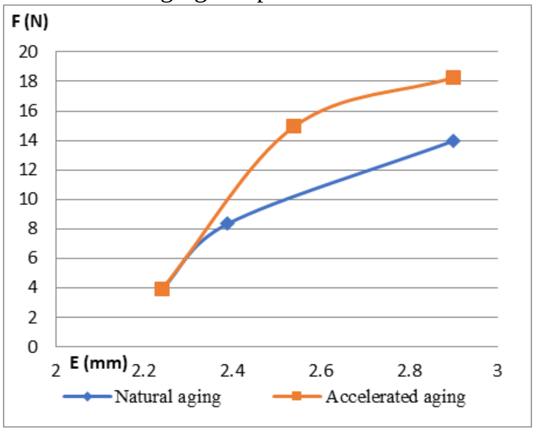


Figure 3. Evolution over time of mechanical properties in the case of naturally aged and accelerated pyrotechnic compositions

This can be explained by the fact that the polyurethane binder used undergoes continuous crosslinking processes, consolidating over time the polymer chain, throughout the entire time of storing of FLARE ammunition, accelerated aging favoring these reactions. The presence of ester groups, double bonds and hydroxyl groups in the polyol chain makes it possible to crosslink it in stages. The presence of the aromatic ring stiffens the chain, while the structure of the triglycerides in the composition of the polyurethane binder maintains the initial flexibility.

At the same time, it is observed that the presence of the oxidizing agent does not influence the preservation of the mechanical resistance of the FLARE type pyrotechnic composition. The binder made of the polyurethane component and the chlorinated rubber has sufficiently stable mechanical properties over time so that no antioxidant additives are required.

The HPLC analyses (Fig. 4 – 6) show a decrease in the concentration of BHT over time, a more pronounced decrease in the case of accelerated aging, according to Table VI.

TABLE VI. BHT CONTENT OF SAMPLES EXPOSED TO AGING

No.	The time at which the analysis was performed	BHT content (%)
1	Initial	1.5573
2	After 3 months of natural aging	1.4215
3	After 6 months of natural aging	1.1001
4	After 3 months of accelerated aging	1.2357
5	After 6 months of accelerated aging	1.0390

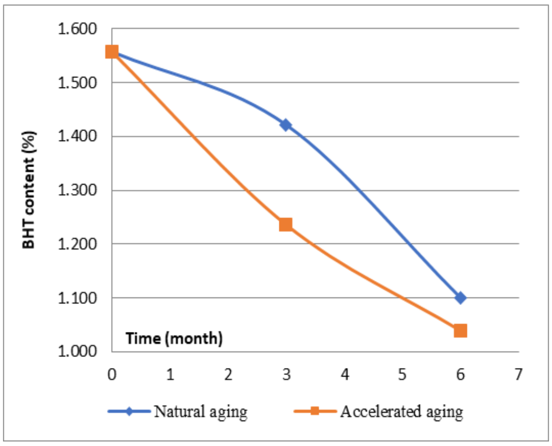
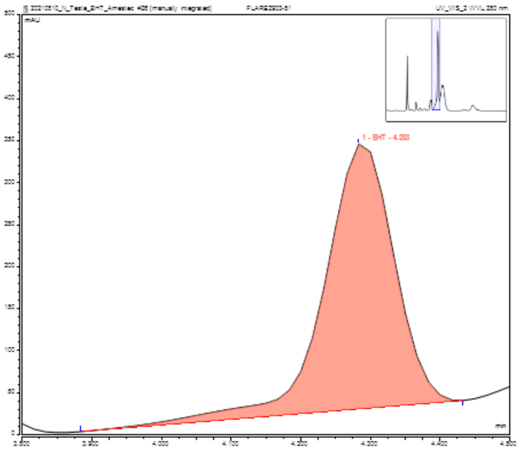
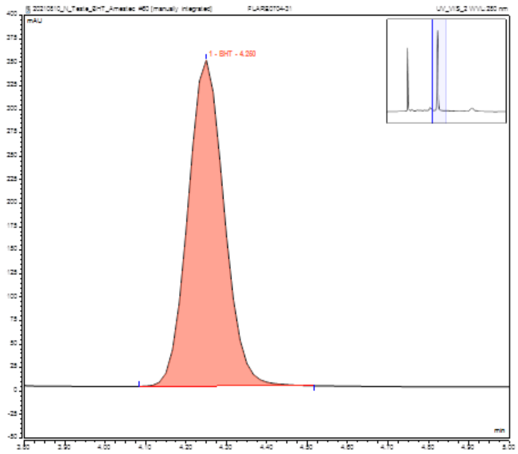


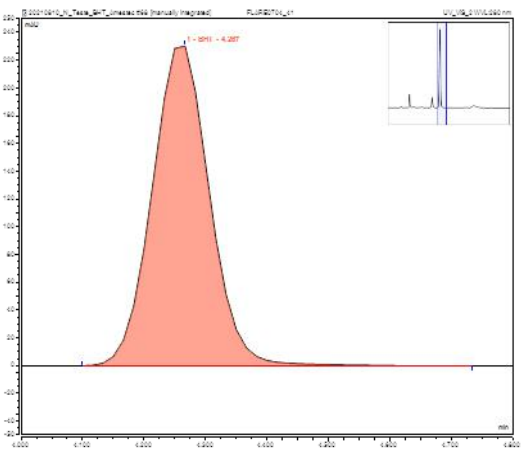
Figure 4. Evolution over time of antioxidant concentration



Initial



After 3 months



After 6 months

Figure 5. LC chromatograms for the initial sample and the naturally aged samples

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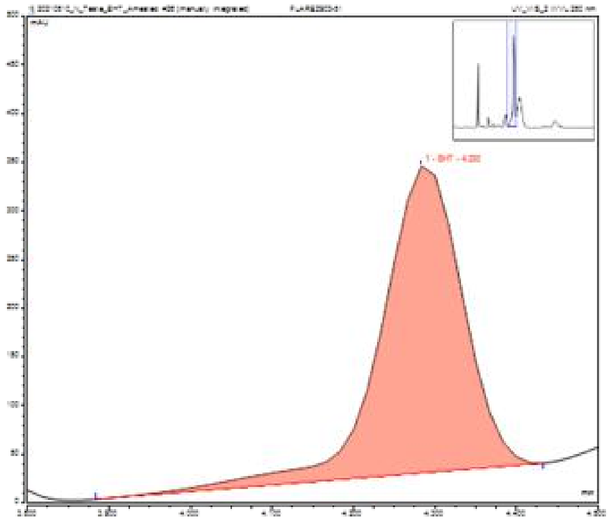
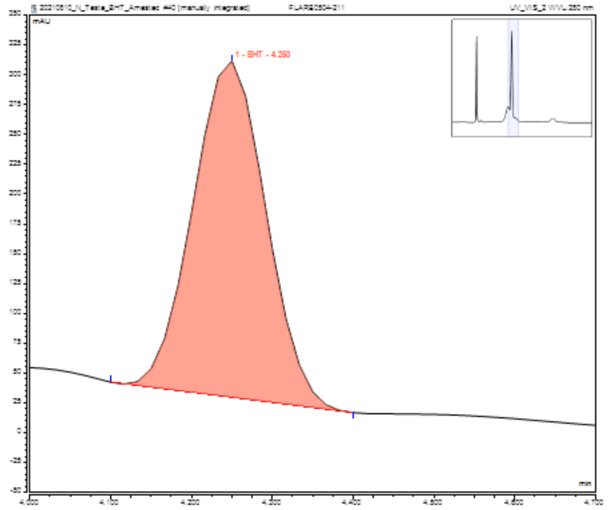
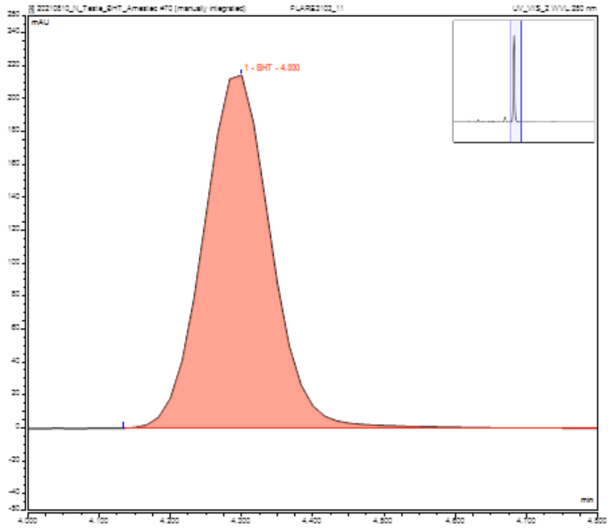


Initial



After 3 months



After 6 months

Figure 6. LC chromatograms for the initial sample and artificially aged samples

IV. CONCLUSIONS

The study presents an experimental method for evaluating the mechanical properties of flare-type pyrotechnic compositions that have been exposed to natural and accelerated aging for 3 and 6 months. It has been shown that the matrix created by the polyurethane binder in combination with the chlorinated rubber in the composition strengthens over time, increasing the uniaxial tensile strength at least three times until it reaches its maximum value and helps maintain mechanical strength throughout the use of ammunition.

At the same time, the use of HPLC analysis technique has shown that, in the case of the above composition, the presence of antioxidants is not necessary to avoid degradation of the binder and increase the life of energetic compositions, as is the case with most formulations of this type. By excluding antioxidants from this kind of formulation, we can reduce the cost of production.

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