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Mechanical Compression Behaviour of "Green" Rocket Propellants

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Abstract. The issues related to mechanical resistance of solid rocket propellants, which can appear during storage or handling of the launching system, are considered to directly influence the burning performance. Thus, in this study, four new types of composite rocket propellants, based on an environmentally friendly oxidizer (phase-stabilized ammonium nitrate), a metallic fuel (aluminium), and a "green" polyurethane-based binder (synthesized from an oligomeric isocyanate and a blend of polyester-polyols obtained through the catalytic degradation of polyethylene terephthalate), were subjected to compression mechanical analysis in order to highlight the importance of the binder on the response given by the tested materials subjected to compressive loads. The samples showed remarkable mechanical performances, the experiments allowing us also to determine the influence of the binder composition and fuel granulation on mechanical properties of the composite propellant.

Keywords: green rocket propellants, mechanical analysis, recycled polyurethane

1. INTRODUCTION

The composite rocket propellant is one of the main energetic components of a missile system, besides the explosive charge. Thus, the structural integrity of the grain propellant is a key factor for projectile efficiency. It is well known fact that in the combustion chamber of a rocket motor, the solid propellant grains are subjected to a variety of loads due to their vulnerability to environmental factors influencing their entire life-cycle, consisting of production, storage, transportation, and ignition [1-3].

The binder, employed in the propellant composition, has the biggest effect on mechanical properties and integrity of the grain. Solid elements represented by oxidizers, metallic fuels, and additives are incorporated into the binder matrix, which ensure homogeneity, protection towards the environment and mechanical characteristics corresponding to the energetic mixture [2-4]. However, mechanical properties are not only influenced by the nature and concentration of the polyurethane binder, but also by the particle dimensions and the concentration of the solid components (oxidizer, metallic fuel, and additives) [5-6].

Considering the composition of a polyurethane matrix (prepolymer, polyols, and curing agents), mechanical properties are predominantly determined by the crosslink density in the binder matrix, which can be adjusted by varying these components [1-4]. These organic compounds react with each other in order to form a polyurethane network structure that makes the matrix softer or harder at the end of the curing process. In this sense, the molar ratios of the reacting species, namely the -NCO:-OH ratio, are important aspects for adjusting the crosslinking density and for obtaining acceptable mechanical properties [1-4]. From a practical point of view, mechanical properties must be customized by varying the -NCO:-OH molar ratios within a narrow interval, so that the heterogeneous mixture developed retains its flowability for a casting process.

This requires experimental studies for evaluation of the effect of -NCO:-OH molar ratios on the mechanical properties of the propellant (amount of binder used). Typically, the amount of binder used in rocket formulations is about 12-15%, the difference being the amount of solids [6].

The issues related to the mechanical performance of solid rocket propellants, which can appear during storage or handling of the launching system, are considered to directly influence the performance and safety of the launching system.

Thus, in this study, four new types of composite rocket propellants based on environmentally friendly oxidizer (phase-stabilized ammonium nitrate), a metallic fuel (aluminum) and a "green" polyurethane-based binder (synthesized from an oligomeric isocyanate and a blend of polyester-polyols obtained through the catalytic degradation of polyethylene terephthalate), were obtained at a laboratory scale and were subsequently subjected to compression mechanical analysis in order to highlight the relationship established between their composition and their mechanical performances.

The mechanical behaviour was evaluated according to the type of binder and the average particles size of the metallic fuel used in the energetic material formulation. Hence, two categories of polyurethanes were investigated independently during the investigation, one was based on commercial polyol, Sethatane®, and the other was based on polyester-polyols derived from recycled polyethylene terephthalate (PET). The samples were cured with a commercial aromatic polyisocyanate, Desmodur® 44V20L. The -NCO:-OH molar ratio of isocyanate to polyols mixture was 3:2. The particles size of the metallic fuel (aluminium powder) was 5 μm and 200 μm, respectively.

2. MATERIALS AND METHODS

The sections below contain technical information on the chemical compounds involved, laboratory equipment, and the synthesis and characterization procedures.

2.1. Materials

The "eco-friendly" oxidizer, phase-stabilized ammonium nitrate (PSAN), was prepared according to the procedure described in the literature [7], where ammonium nitrate (AN, min. 99%, Honeywell Fluka™) and potassium nitrate (KN, 99%, ACROS Organics™) were co-crystallized from an aqueous solution. The polyester-polyol (named RP1), resulted from PET degradation, was vacuum dried for 24 hours at 50°C and subsequently used for the synthesis of polyurethane [8].

Commercial polyol, Setathane D1160, -OH content 5.4%, (SET, Allnex) and curing agent, diphenylmethane–4,4′–diisocyanate, -NCO content 31.5% (MDI, technical product Desmodur® 44V20L, Covestro) were vacuum dried for 24 h at 50°C before being employed. As metallic fuel, two types of aluminum powder, with an average particle size <5 µm (99.5%, Sigma Aldrich) and 200 µm (99.5%, Sigma Aldrich), were used as received. As burning catalyst, iron oxide (99.9%, powder, Fe_2O_3, Sigma Aldrich) was employed as received.

2.2. Methods

2.2.1. Rocket composite propellant development

Rocket composite propellant formulations are heterogeneous compounds consisting of a polymer matrix and a solid load. At the beginning, the binder is in liquid state (components MDI:SET:RP1) and incorporates the solids, consisting of oxidizer (PSAN), metallic fuel (Al), and catalyst agent (Fe_2O_3). Table 1 provides data on a polyurethane composition and a molar ratio of isocyanate to polyols.

Table 1. Composition of the polyurethane used in rocket propellant formulations

Sample	**Composition**	**-NCO/-OH Ratio**
PU_32	MDI:SET	3:2
Sample	**Composition**	**-NCO/(-OH^{SET}/OH^{RP})^1 Ratio**
PU_232	MDI:SET: RP1	3:1.5:0.5

[1]-OH molar ratios for SET and RP1 blends

Starting from the definition of the composite rocket propellants and considering the composition of the polyurethane binders used, the preparation process was carried out in several steps. Firstly, the solid components (oxidant-metallic fuel-catalyst) were mixed until complete homogenization. To obtain good mechanical strength and to facilitate the mixing process, the oxidizer used in the development procedure was bi-granular (200 µm and 50 µm). The particles size of the metallic fuel (aluminum powder) was 5 µm and 200 µm, respectively. Secondly, the previously developed solids mixture was added to the polyols blend and mixed until homogenous state. To improve the processability, the mixing process was carried out at 50°C. Finally, the resulting compounds were cured with a commercial aromatic polyisocyanate, Desmodur® 44V20L. The -NCO:-OH molar ratio of isocyanate to polyols mixture was 3:2, as depicted in Table 1. The developed compositions were subsequently introduced into cylindrical molds with 20 mm diameter and they were allowed to harden at 60°C for 96 hours in a vacuum oven.

The cured samples were recovered from the molds after the curing process was completed and they were subjected to compressive investigation as described in the next section. Regarding small amount of the developed composition, the mixing process was performed on a Thinky Mixer ARE-250 CE. The described procedure can be better understood in conjunction with the illustrations presented in Fig. 1. The rocket propellant formulations are depicted in Table 2.

Table 2. Formulations for the rocket propellant composite

Sample	Components [wt.%]							Density [g/cm^3]
	PU_32	PU_232	PSAN		Fe_2O_3	Al <5 µm	Al 200 µm	
			50 µm	200 µm				
ECP_32S	15		20	52	1	12		1.51
ECP_32B	15		20	52	1		12	1.44
ECP_232S		15	20	52	1	12		1.50
ECP_232B		15	20	52	1		12	1.43

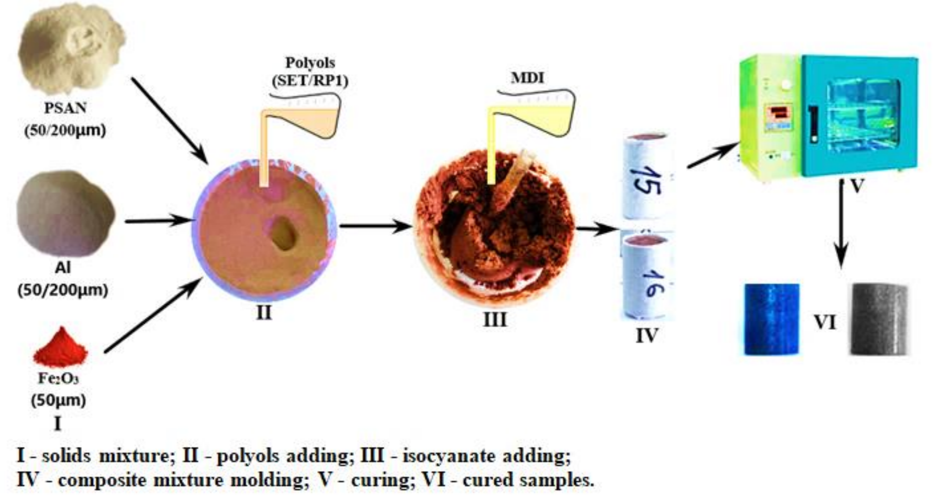

Fig. 1. Schematic representation of the "green" rocket propellants development process

2.2.2. Rocket composite propellant characterization

To investigate the possibility of employing these novel types of polyurethanes as binders in rocket propellant composites, the developed formulations were a subject to mechanical analysis. The low strain rate compression investigations of the developed composite rocket propellants were performed on an Instron 2519-107 Universal Test Machine (Instron, Norwood, MA, 02062-2643, USA), where cylindrical specimens, with a diameter of 20 mm and a length of 20 mm, were tested at a compression rate of 50 mm/min.

For each sample, the test was repeated three times, to observe the repeatability of mechanical behaviour. The investigation was carried out at ambient temperature.

3. RESULTS AND DISCUSSIONS

Compression deformation at the breaking point of the developed composite propellants, as a function of a binder type and a metallic fuel particle size, is illustrated in Fig. 2. To obtain accurate data on mechanical behaviour, during the uniaxial compression tests, the percentage of binder and fuel used was the same for all samples.

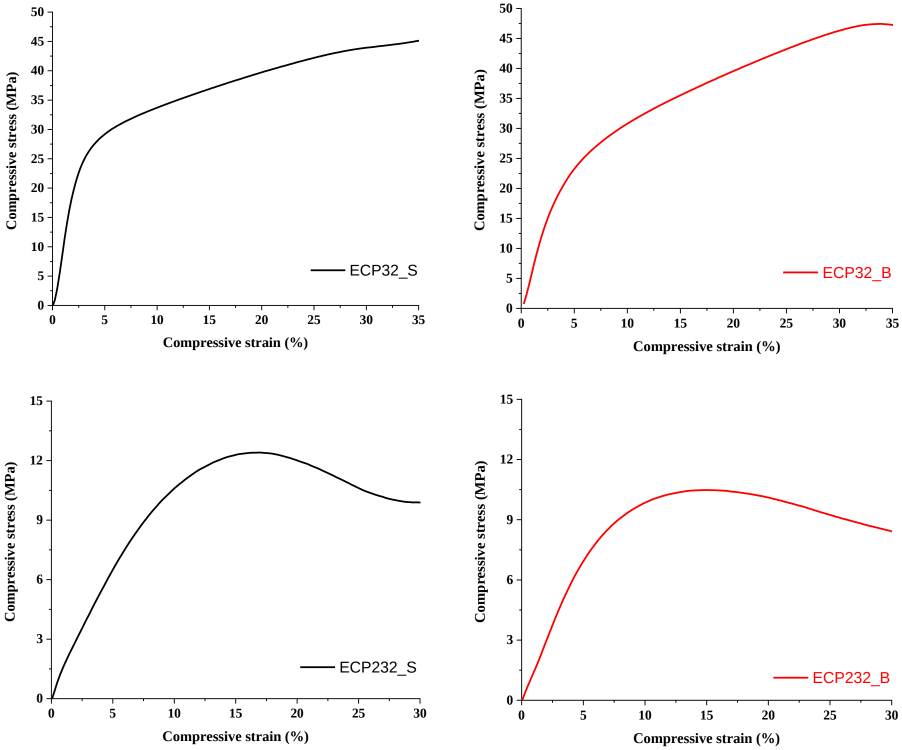

Fig. 2. Compressive stress–strain profiles of composite rocket propellants

The compressive strength of the samples appears to be directly influenced by the fuel's particle size and type of the binder used. Thus, the most rigid and resistant sample is ECP32_S, due to use of commercial polyol and small particles (<5 µm), followed by ECP32_B, based on large particles (200 µm). Comparing formulations with a similar particle size, the stress–strain differences appear due to the use of recycled polyurethane.

Therefore, ECP32_S and ECP32_B showed a compressive stress resistance three times higher than that of ECP232_S and ECP232_B, respectively. This aspect can be observed in Table 3, where the values of the yield and fracture stress points are displayed. The grain size of the metallic fuel had a low impact on mechanical resistance of the propellant grains, compared to the influence provided by the type of polyurethane used. Even if the composite rocket propellants, based on the recycled binders, displayed lower resistance to compression, their plasticity may represent an advantage in some circumstances because there is lower probability for them to crack.

Mechanical behaviour of "green" polymeric mixtures, developed by introducing these new types of binders based on recycled PET, provides an ideal background for more comprehensive tests to demonstrate their applicability as alternatives to rocket propellants.

Table 3. Compressive strain–stress values of the composite rocket propellants

Sample	**Yield**		**Fracture**	
	Strain [%]	**Stress [MPa]**	**Strain [%]**	**Stress [MPa]**
ECP32_S	2.77	23.64	30.57	44.04
ECP32_B	2.70	16.12	33.23	47.43
ECP232_S	4.92	7.01	16.38	12.44
ECP232_B	4.90	6.89	14.65	10.47

The structural degradation of the cylindrical composites during the compressive testing is illustrated in Fig. 3.

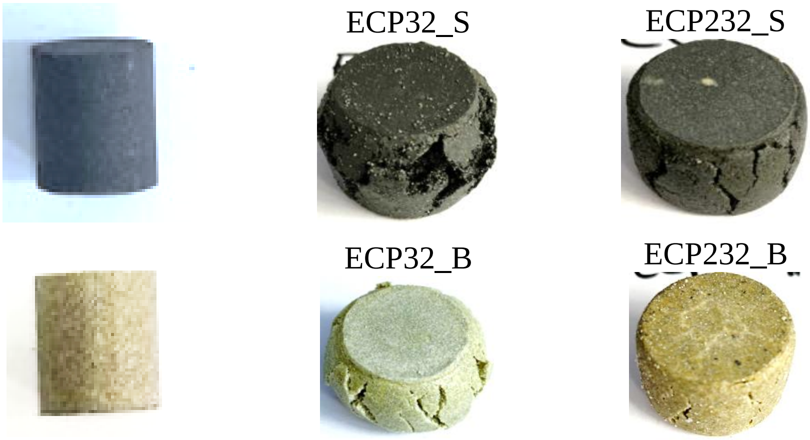

Fig. 3. The structural configuration of cylindrical composites after testing (left: specimens before compressive loading application; middle and right: specimens after compression testing)

4. CONCLUSIONS AND PERSPECTIVES

A new category of polyurethane binders, based on polyester-polyol obtained from the catalytic degradation of recycled PET, a commercial polyol and an aromatic isocyanate, were investigated as their applications in future composite rocket propellants. Thus, to see that this new "green" approach is suitable for this type of application compared to state-of-the-art HTPB binders (currently widely used in this field), the developed composite mixtures were subjected to compressive mechanical analysis.

The compression test results showed that the developed composite rocket propellant samples possess acceptable mechanical behaviour. Comparing these with the existing HTPB and the commercial binders currently used in rocket propellants, despite their weaker mechanical strength, the binders based on recycled PET waste open the background for further studies in the future.

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