

The use of image analysis for the study of interfacial bonding in solid composite propellant

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Abstract: In the framework of this research, the program Image Pro Plus was applied for determining the polymer–oxidizer interactions in HTPB-based composite propellants. In order to improve the interactions, different bonding agents were used, and their efficiency was analyzed. The determination of the quantity, area and radius of non-bonded oxidizer crystals is presented. The position of formed cracks in the specimen and their area have a great influence on the mechanical properties of composite propellant. The preparation of the composite propellant in order to enable the photographing of their structure by means of stereoscopic and metallographic microscopes with the digital camera is also described as well.

Key words: composite propellant, interactions, grain distribution, dewetting, image analysis, mechanical properties.

INTRODUCTION

Image Pro Plus is a software package used for image acquisition, enhancement and analysis. Image data can be enhanced using a large variety of color and contrast filters. Image Pro Plus enables users to trace and count objects manually or automatically. The attributes of objects, such as length, area, diameter and angle, can be measured and the image can be calibrated to the desired unit of measure.¹

Within the framework of this research, the program Image Pro Plus was employed for the determination the interactions between the components of solid composite materials.

Modern composite propellants are heterogeneous powders (mixture), which use a crystallized or finely ground mineral salt as an oxidizer (often ammonium perchlorate), which constitutes between 60 and 90 % of the mass of the propellant. The fuel itself is aluminum. The propellant is held together by a polymeric binder (usually polyurethane or polybutadiene). The final products are rubber like substances, with the consistency of a hard rubber eraser.

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Composite propellants require certain interactions between the polymer and filler (oxidizer and metal component) in order to prevent separation around a particle of filler. If dewetting occurs between the binder and filler, the flame front propagates below the burning surface to produce a more rapid combustion of the propellant.² This would have two undesired consequences: an increase of the pressure in the rocket engine and creation of cracks, which may cause detonation during the combustion process.

Poor interactions between binders and fillers are found mostly with oxidizers and not with the metal fuels. The metals are not a problem, because metals have a more irregular surface and a greater ease for chemical bonding with the filler.² On the other hand, oxidizers have surfaces which are very smooth and, in some cases, the oxidizers do not chemically bond with the filler.

Attempts to improve the binder–filler interactions in composite propellants have included the addition of a bonding agent. A bonding agent produces an interaction between the oxidizer crystal and the binder by forming either primary or secondary bonds with the oxidizer and a primary bond with the binder.³

In addition, the role of bonding agents is to facilitate the formation of propellants through decreasing the viscosity of the emulsion and to improve the physical and mechanical properties of the propellant by preventing adhesion of the binder to the solids, thereby decreasing its tensile strength. Thus, bonding agents play a double role, serving as a wetting agent for the solids and increasing the cohesion between the binder and the solids.

The bonding agents used in this research were functionally substituted isocyanurates, which are universal bonding agents, and can be used for all binder–filler systems (Fig. 1).

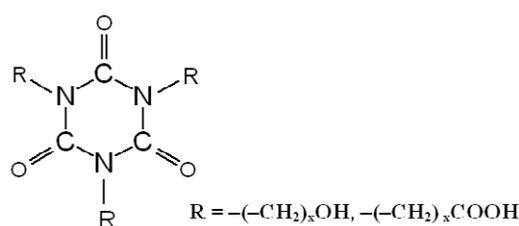


Fig. 1. The studied 1,3,5-trisubstituted isocyanurates.

Selection of R was based on the binder and the reactivity of R therewith. The R functional group of the bonding agent must be reactive or compatible with and is preferably the same as the functional group on the binder.⁴

Interactions between two ingredients are improved with an even distribution of ammonium perchlorate (AP) particles. If the bonds between polymer and filler are not very strong, dewetting will occur. By determining the area and diameter of non-bonded AP particles, the efficiency of bonding agents in providing binder–filler interactions can be assessed.

So far, no polymeric binder material has been found which prevents moisture from diffusing into the interior of the propellant grain. Although moisture at ordinary temperatures does not undergo chemical reaction to any significant degree with the components of the propellant, it nevertheless, strongly affects the mechanical properties. This deterioration of the properties is caused by the accumulation of moisture on the surface of the oxidizer crystals, thus creating a low modulus (liquid) layer which envelops the particle. In essence, this means that the "bond" between the oxidizer and binder is destroyed and dewetting will commence at low stress levels with commensurate loss of mechanical properties.⁵ The area of the cross section of cracks and their position in the specimens are good indicators of mechanical properties.

The topic of this study was to establish the conditions of the preparation of composite propellants containing ammonium perchlorate (AP), hydroxyl terminated polybutadiene (HTPB) and 1,3,5-trisubstituted isocyanurate as bonding agents. The bonding phenomenon was investigated by the stereoscopic and metallographic microscopes with a digital camera. The morphological characteristics of the images obtained were analyzed using Image Pro Plus software package.

EXPERIMENTAL

Synthesis of 1,3,5-trisubstituted isocyanurates

Tri(2-carboxyethyl) isocyanurate was obtained by reacting cyanuric acid with a molar excess of acrylonitrile in the presence of a strongly alkaline catalyst (trimethylphenylammonium hydroxide) and in a reaction medium containing a suitable solvent (dimethylformamide) for the reactants and the intermediate product tri(2-cyanoethyl) isocyanurate which is formed. The tri(2-cyanoethyl) isocyanurate was hydrolyzed to the corresponding tri(2-carboxyethyl) isocyanurate by heating them to boiling with an aqueous mineral acid according to a modified literature procedure.^{6,7}

Tri(2-hydroxyethyl) isocyanurate was prepared by the reaction of cyanuric acid and 2-chloroethanol in alkaline medium, according to literature data.⁸

The synthesized 1,3,5-trisubstituted isocyanurates were identified by their melting points and FTIR, ¹H-NMR and UV spectroscopic data.

Ammonium perchlorate and hydroxyl-terminated poly(butadiene) were obtained from Fluka and Arco Chemical.

Preparation of the composite propellants

Specimens containing ammonium perchlorate (AP), hydroxyl-terminated polybutadiene (HTPB) and different trisubstituted isocyanurates as bonding agents, in a weight ratio of 7:2:1 were prepared.

Specimen No. 1 contained tri(2-carboxyethyl) isocyanurate, while specimen No. 2 contained tri(2-hydroxyethyl) isocyanurate as bonding agents. These bonding agents are abbreviated as BA I and BA II, respectively.

Propellant paste was made in the laboratory in a 10 g scale. Active coal was added to the bonding agent, and the mixture was homogenized in a stamp mortar. Sufficiently dried ammonium perchlorate (AP) was added, the mixture was placed in a beaker and HTPB was added. The paste was mixed with the help of a spatula inside the beaker for about one minute. This phase was followed by homogenization designed to improve the wetting of the solids by the binder and to decrease the viscosity to the point where casting could be performed under good conditions. In the next phase the propellant sample mixture was shaped in order to obtain a sample pellet, after which the pellet was maintained at 60 °C for 48 h.^{7,9}

Analysis of composite samples

The first obtained specimen was hard, but it crumbled during cutting (Fig. 2). The uncured mixture was typically dough-like. Trapped air, creating voids in the grains, could cause problems.

The obtained second specimen was jelly-like and stuck to the employed tools, which was complicated the preparation for image analysis (Fig. 3).

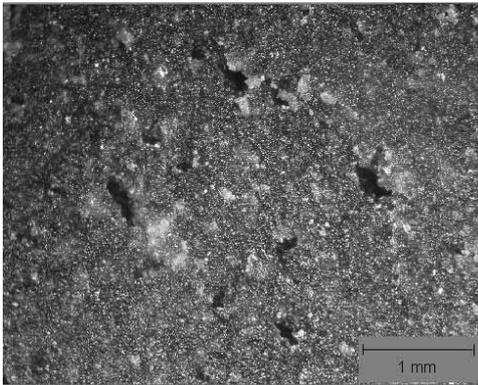


Fig. 2. Micrograph of the composite specimen No. 1.

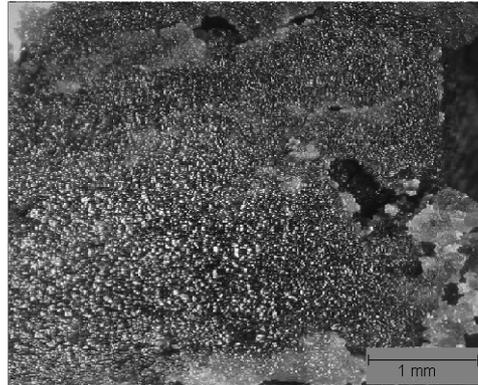


Fig. 3. Micrograph of the composite specimen No. 2.

RESULTS AND DISCUSSION

The obtained composites were photographed using the stereoscopic and metallographic microscope with the digital camera, and images obtained were analyzed using program Image Pro Plus.

AP Distribution

When small amounts of active coal were introduced into the composite propellant, all ingredients became colored, except AP which maintained its natural color. Using Image Pro Plus, the observed change in color was utilized to determine the percentage of AP particles and their distribution. In order to determine distribution of AP, the specimens were divided into several segments.

The distribution of AP in specimen No. 1 and 2 is presented in Table I.

TABLE I. Distribution of AP in specimen No. 1 and 2

Segment	Area, mm ²		AP Area, mm ²		AP Ratio, %	
	1	2	1	2	1	2
I	2.5781	3.6655	1.4600	2.1413	56.6321	61.7900
II	2.1512	3.3445	1.4647	2.1635	68.0883	64.6881
III	1.8443	3.2145	1.1124	1.6504	60.3122	51.3434
IV	2.8190	3.1422	1.9036	2.1621	67.5247	64.6912
V	2.4058	–	1.4057	–	58.4292	–
VI	1.8689	–	1.1977	–	64.0877	–

The obtained results show that AP particles were nearly equally distributed and their ratio ranged from 58 to 69 % in specimen No. 1 and from 51 to 65 % in specimen No. 2. Although this distribution has a great influence on the interactions between polymer and oxidizer, the process of dewetting has a dominant influence on binder–AP interactions.

Binder–AP interactions

If the bonds between the binder matrix and the oxidizer are not very strong, dewetting occurs and halos are formed in the vicinity of the oxidizer.

In order to assess the influence of bonding agent on the binder–AP interactions, two specimens containing different bonding agents were used. By determining the quantity, area, radius and roundness of non-bonded AP particles, significant information about binder–filler interactions can be gained. The determined parameters for the specimen containing BA I (specimen No. 1) are given in Table II.

TABLE II. Statistics for specimen No. 1

	Area, μm^2	Diameter (max), μm	Diameter (min), μm	Holes	Roundness
Min	20.576	5.1230	5.1230	0	1
Max	22530.0	250.07	126.45	0	147.28
Range	583.07	28.202	13.917	0	3.8367
Sum	60640.00	2933.00	1447.4	0	399.02
Samples	104.00	104	104	104	104

The grain size distribution and area distribution is significant, because AP particles are agglomerated into clusters. According to the different area, non-bonded APs are classified into three classes, Table III.

TABLE III. Area classification for specimen No. 1

Class	Objects	Objects, %	Area (mean), μm^2	Diameter (mean), μm	Roundness (mean)
1	102	98.077	271.852	18.476	1.160
2	1	0.9615	10380.6	124.02	2.737
3	1	0.9615	22530.0	196.74	2.595

From the obtained results it can be noticed that the specimen contains a large percentage of non-bonded AP particles. The discrete AP particles (102 objects) had nearly orbicular configurations (roundness around 1), while the clusters (2 objects) had irregular conformations. Clusters formation has a negative influence on binder–filler interactions.

The formation of halos in specimen No.1 can be interpreted as the failure of the adhesive bond between the binder matrix and oxidizer. Before dewetting, tiny voids were created next to the AP particles, but distinctly located in the matrix, away from the AP surface.¹⁰ After further straining, these voids coalesce and merge into vacuoles, exposing the oxidizer surface, Fig. 4. The dewetted particles exhibit a typical eye-texture.

The determined parameters for the specimen containing BA II (specimen No. 2) are given in Table IV.

TABLE IV. Statistics for specimen No. 2

	Area, μm^2	Diameter (max), μm	Diameter (min), μm	Holes	Roundness
Min	62.011	8.712	8.163	0	1.000
Max	193.43	16.012	13.744	0	1.046
Range	117.60	12.070	10.845	0	1.010
Sum	2116.7	217.25	195.22	0	18.178
Samples	18	18	18	18	18

Only a small percentage of non-bonded AP particles was observed and it can be concluded that very strong bonds between the polymer binder and oxidizer prevent dewetting, Fig. 5.

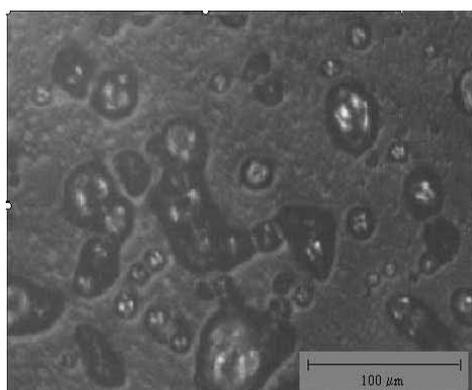


Fig. 4. Cavity formation around non-bonded AP crystals in specimen No. 1.

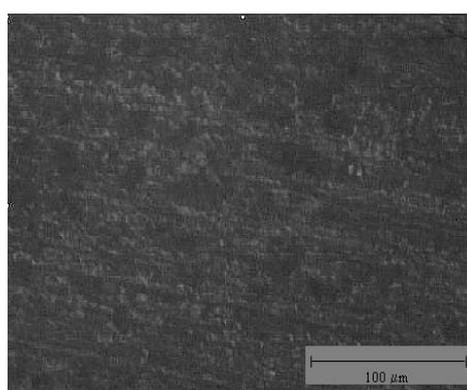


Fig. 5. AP Crystal bonded to the polymer matrix in specimen No. 2.

The minority of non-bonded particles can be classified into three groups, Table V.

Table V. Area classification for specimen No. 2

Class	Objects	Objects, %	Area (mean), μm^2	Diameter (mean), μm	Roundness (mean)
1	2	11.111	65.482	8.583	1
2	4	22.222	83.877	9.717	1
3	12	66.667	137.520	12.561	1.015

For each class, minor differences between the radius and area of the particles are observed, and it can be inferred that the AP particles had the same area and grain size. Particle agglomeration was not observed. Further evidence that the AP particles were non-agglomerated is that the roundness had a value around 1 for every class.

Crack cross section

During the synthesis of HTPB based propellants with tri(2-carboxyethyl) isocyanurate as the bonding agent, trapped air can be a problem, creating voids in the grains. Likewise, voids and bubbles can result from gases evolved during curing as a result of moisture absorption. This results in crack formation. The area of the cross section of the cracks was 0.2679 cm^2 , which was 1.96 % of the overall surface area of the sample. All the cracks occurred in the interior of the sample and they occupied a considerable part of the sample area, Fig. 6.

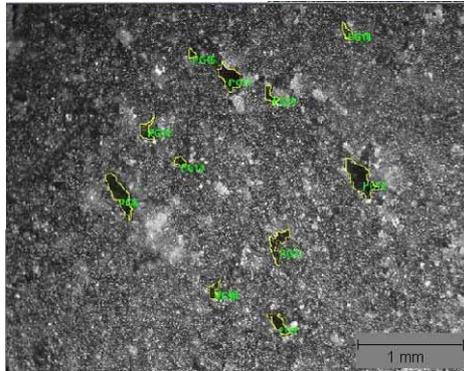


Fig. 6. Micrograph of crack formation.

Crack formation can lead to bad mechanical properties, but during the preparation of the specimens, this drawback can be eliminated.

In the HTPB based propellant with tri(2-hydroxyethyl) isocyanurate as bonding agent, no crack formation was found, hence the specimen had better mechanical properties compared to the specimen No. 1.

These results are in accordance with previous investigations⁷ of the interactions between ammonium perchlorate, different bonding agents and hydroxyl-terminated poly(butadiene), studied by means of the FTIR spectroscopic method. It was shown that the interfacial bonding force arises from hydrogen bonding in the case of tri(2-hydroxyethyl) isocyanurate. This effect was not observed when tri(2-carboxyethyl) isocyanurate was used as the bonding agent.

CONCLUSION

Based on the analysis of the experimental results, the following conclusions can be deduced:

- In HTPB based propellants with tri(2-carboxyethyl) isocyanurate as the bonding agent, the AP particles were nearly equally dispersed in the polymer binder, but there was a large percentage of non-bonded AP particles, which were generated during dewetting. The non-bonded AP particles were agglomerated, probably because of deficient homogenization during the preparation of the specimens. During synthesis, trapped air was a problem, creating voids in the grains. This resulted in crack formation, which covered 1.93 % of the overall surface area of the sample.

- In HTPB based propellants with tri(2-hydroxyethyl) isocyanurate as the bonding agent, the AP particles were nearly equally distributed in the polymer binder. Only a small percentage of non-bonded AP particles was observed, from which it can be concluded that very strong bonds between polymer binder and oxidizer prevented dewetting. The mechanical properties were better compared to the first specimen, because no crack formation was found. The drawback of this specimen was its stickiness, which complicated the preparation for image analysis.
- The effects of the bonding agents in improving the interactions between polymer and AP were significant when tri(2-hydroxyethyl) isocyanurate was employed.
- The effects of tri(2-carboxyethyl) isocyanurate as bonding agent were negligible in improving the interactions between polymer and filler.
- Tri(2-carboxyethyl) isocyanurate as bonding agent does not have a great influence on improving the AP–polymer interactions.

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ИЗВОД

КОРИШЋЕЊЕ АНАЛИЗЕ СЛИКЕ ЗА ОДРЕЂИВАЊЕ ИНТЕРАКЦИЈА У ЧВРСТИМ КОМПОЗИТНИМ ГОРИВИМА

ЈАСМИНА ДОСТАНИЋ, ГОРДАНА УШЋУМЛИЋ, ТАТЈАНА ВОЛКОВ–ХУСОВИЋ,
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У оквиру истраживања програм Image Pro Plus је примењен за одређивање интеракција између полимера и оксиданса у композитним горивима на бази НТРВ. У циљу побољшања ових интеракција, коришћени су различити везујући агенси и анализирана је њихова ефикасност. У раду је такође вршено одређивање количине, удела, површине и пречника честица, које нису везане за полимер. Површина формираних пукотина и њихова расподела у узорку имају велики утицај на механичка својства композита. Припрема узорака композитних горива за снимање њихове морфолошке структуре помоћу стереомикроскопа и метаграфског микроскопа са дигиталном камером је такође описана.

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