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UTICAJ TEHNOLOGIJE UVOĐENJA PLASTIFIKATORA U SMEŠU LIVENOG KOMPOZITNOG EKSPLOZIVA NA PROCESNA SVOJSTVA

INFLUENCE OF THE TECHNOLOGY OF INTRODUCING PLASTICIZER IN THE MIXTURE OF CAST COMPOSITE EXPLOSIVE ON THE PROCESSING PROPERTIES

Danica Bajić*[1,2], Mladen Timotijević[1], Mirjana Krstović[12], Aleksandar Milojković[1], Slavko Mijatov[1]
[1]Vojnotehnički institut, Beograd
[2]Univerzitet odbrane, Vojna akademija, Beograd

U formulacijama livenih kompozitnih eksploziva sa polimernim vezivom plastifikatori se, kao aditiv, najčešće dodaju polimernom vezivu na početku mešanja radi smanjenja viskoziteta, potpunije homogenizacije i radi lakšeg livenja samog eksploziva nakon homogenizacije. Pored značajnog uticaja koji imaju na reološko ponašanje smeše, njihovo prisustvo ima uticaj na kasnije mehaničke karakteristike eksploziva nakon očvršćavanja. Pored prakse da se plastifikator u smešu uvodi dodavanjem u polimerni premix, postoji opcija da se uvede naknadno, kao flegmatiyator prisutan na česticama nitraminskog eksploziva. Naime, nitramini poput oktogena i heksogena, često se, radi bezbednog transporta, flegmatizuju tj. oblažu malom količinom plastifikatora, kao što su izodecil pelargonat, dioktil adipat, dioktil sebacat itd. Tada nije potrebno u konačnu eksplozivnu smešu dodavati plastifikator, već se računa na onu količinu koja je već prisutna uz nitraminsku komponentu. U ovom radu ispitan je uticaj tehnologije inkorporiranja plastifikatora - dioktil adipata u višekomponentni liveni kompozitni PBX eksploziv. Analizirana su 2 slučaja: kada je dioktil adipat dodat u polimerni premiks pre dodavanja čvrstih komponenti eksplozivne formulacije, i kada je dioktil adipat dodat zajedno sa oktogenom kao nitraminskom komponentom. Za eksperimentalne sastave livenog kompozitnog eksploziva sa dioktiladipatom uvedenim u smešu na dva prethodno opisana načina izvršena su poredbena ispitivanja sledećih svojstava: vremenska zavisnost prividnog viskoziteta, zatezna čvrstoća, gustina i tvrdoća. Primećene su razlike u ovim svojstvima koje mogu da utiču na procesibilnost ovih eksplozivnih formulacija i njihovu dalju primenljivost.

Ključne reči: *liveni kompozitni eksplozivi; plastifikator; viskoznost; fizičko-mehanička svojstva; procesna svojstva*

In the formulations of cast composite explosives with a polymer binder, plasticizers, as an additive, are most often added to the polymer binder at the beginning of mixing in order to reduce viscosity, more complete homogenization, and for easier casting of the explosive itself after homogenization. In addition to the significant influence they have on the rheological behavior of the mixture,

* Corresponding author: danica.bajic@mod.gov.rs
https://orcid.org/0000-0002-2170-1995

Mladen Timotijević: https://orcid.org/0009-0001-7650-9028
Mirjana Krstović: https://orcid.org/0000-0002-5469-3581
Aleksandar Milojković: https://orcid.org/0000-0002-0330-3627
Slavko Mijatov: https://orcid.org/0000-0001-8512-5088

their presence has an impact on the subsequent mechanical characteristics of the explosive after curing. In addition to the practice of introducing the plasticizer into the mixture by adding it to the polymer premix, there is an option to introduce it subsequently, as a phlegmatizer present on the nitramine explosive particles. Namely, nitramines such as octogen and hexogen are often, for the sake of safe transport, phlegmatized - coated with a small amount of plasticizers, such as isodecyl pelargonate, dioctyl adipate, dioctyl sebacate, etc. In that case, it is not necessary to add a plasticizer to the final explosive mixture, but it is calculated on the amount that is already present with the nitramin component. In this paper, the impact of the technology of incorporating the plasticizer - dioctyl adipate into the multi-component cast composite PBX explosive was examined. Two cases were analyzed: when dioctyl adipate was added to the polymer premix before adding the solid components of the explosive formulation, and when dioctyl adipate was added together with octogen as a nitramine component. For the experimental compositions of cast composite explosives with dioctyl adipate introduced into the mixture in the two previously described ways, comparative tests of the following properties were performed: time dependence of apparent viscosity, tensile strength, density and hardness. Differences in these properties have been observed that can affect the processability of these explosive formulations and their further applicability.

Key words: *cast composite explosives; plasticizer; viscosity; physical-mechanical properties; processability*

1. Introduction

Plasticizers are regularly added to the formulations of cast composite explosives of type PBX (plastic bonded explosives) or cast composite rocket propellants (CRP) with polymer binder in order to adjust their rheological behavior during the homogenization and casting [1-3]. Their presence has further effect on the mechanical properties after the solidification, as well as on ageing properties of the explosive or the propellant [4]. Modern PBX and CRPs consist of some inert or energetic polymer binder with appropriate additives, among which the plasticizer, and solid energetic ingredients [3, 5].

Plasticizers are most often some nonvolatile chemicals that have low molecular weight and are added to composite materials in order to improve their processability as well as flexibility of the final product [6]. The mechanism of their action is based on the fact that the molecules of a plasticizer form secondary bonds to polymer chains and spread them apart, so that the molecules of plasticizers reduce polymer-polymer chain secondary bonding. This further results in higher degree of mobility for the macromolecules, providing a softer mass, easier to deform [6]. They are lowering viscosity and the temperature of the glass transition of a polymer material or a composite with a polymer binder. Some of often used plasticizers in PBXs and CRPs are isodecyl pelargonate, diocyl adipate, dioctyl phtalate, dibutyl phthalate, etc. Being small molecules, plasticizers may have the ability to migrate over time troughout the solidified charge [7].

There are several possibilities to introduce the plasticizer into a PBX or CRP mixture, and the most often approach is to add the plasticizer on the beginning of the formulation homogenization, i.e. to pour it in the pre-polymer premix. There is also a possibility, when PBX formulations are prepared, to add it together with nitramine explosive, when the plasticizer is used as a phlegmatizing coating on the nitramine explosive crystals. This may be the case when hexogene, RDX, or octogene, HMX are bought coated with a plasticizer for the sake of safe transportation, storage and handling. In this research a comparison was made between the quality and processability of a selected PBX formulation with diocyl adipate, DOA, as a plasticizer incorporated in both the abovementioned methods.

2. Materials and methods

2.1. Cast composite explosive preparation

A selected composition of cast composite PBX explosive HMX/AP/Al/HTPB was manufactured in a batch technology, with two different approaches of plasticizer introduction to the mixture. The explosive formulations were prepared using the following raw materials:

- HMX class 1 (provided by Prva Iskra Namenska, Barič),
- DOA (provided by Trayal Corporation),
- HMX class 1 coated with 3wt.% DOA (Prva Iskra Namenska, Barič),
- ammonium perchlorate (Trayal Corporation),
- aluminium powder (Trayal Corporation),
- polymer binder based on HTPB cured with IPDI.

The homogenization of the ingredients was done in a vertical kneading machine HKV Propex, at 60°C, with vacuum system, to avoid the appearance of air bubbles in the cast charges, i.e. to achieve better particles packaging.

Two batches were produced under the same technological parameters, first with DOA added in the premix, and the second with DOA already present on HMX. The calculation of the ingredients quantity for batches was adjusted to have the same content of DOA in both mixtures, but the calculation was done according to DOA content on HMX, so in the batch with DOA coated HMX, no additional DOA was needed. Order of ingredients incorporation into the PBX mixtures for the two batches is given in Table 1

Table 1. Order of ingredients incorporation into the PBX mixture

Order of dosage	Batch label	
	Batch 1	Batch 2
1	premix: HTPB + DOA	premix: HTPB
2	Al	Al
3	HMX	DOA coated HMX
4	AP	AP
5	IPDI	IPDI

2.2. Characterization methods

For the two prepared batches of PBX, after the homogenization of the mixtures, the apparent viscosity increase with time was observed. This measurement was performed using a Brookfield rotational viscometer RVT, with T-C spindle that was set to rotate with 5 rpm. Viscosity change with time was observed at the temperature of 60°C, in order to determine if there are any differences in curing kinetics between the two mixtures.

After the 120h time of curing – solidification, the density of the cured PBXs was determined according to method MIL 286 C, using Mohr's balance, in 2-propanol, at room temperature (20°C).

Hardness of the solidified explosive samples was measured using a Zorn Stendal DDR device for hardness measurement in Shore A scale. Three measurements were performed per sample, to determine mean value of hardness at room temperature.

Single axis tensile test was carried out on universal testing machine INSTRON 1122. From the solidified PBX blocks the appropriate specimens were cut-out (JANNAF type, dumbbell-shape). Speed of the clamps was 50 mm/min and the test was done at three temperature points within the range of possible exploitation conditions: at -30°C, +20°C and +50°C. Preparation of the specimens for the tensile test, a specimen in the clamps of the testing machine and specimens after this test are shown in Figure 1.

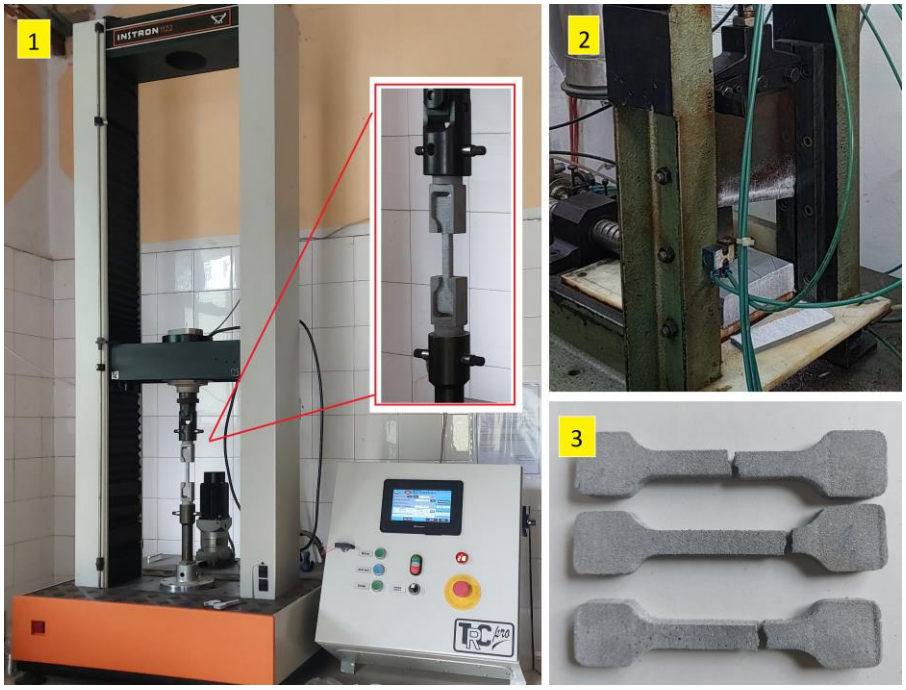

Figure 1. Tensile test: 1 – specimen of PBX in the clamps of the testing machine, 2- preparation of the specimens for the tensile test on a cutting tool, 3- appearance of the specimens after the test

3. Results and discussion

3.1. Rheological behavior

The results of the apparent viscosity measurement at defined points of time after the homogenization are given in Table 2, and graphically presented in Figure 2.

Table 2. Apparent viscosity change in time

Time, min	Apparent viscosity [Pas]						
	15	30	45	60	75	90	105
Batch 1	68.8	70.4	73.6	80.0	86.4	94.4	100.8
Batch 2	73.6	80.0	86.4	97.6	104.0	110.4	115.2

We may observe a moderate increase of the apparent viscosity values in time for both the tested batches. This certainly confirms that the chemical reaction of cross-linking (curing) of the polymer binder is taking place, i.e. that the process of the explosive solidification begun. However, there is a clear difference between the two viscosity curves: the mixture containing DOA-coated HMX had higher viscosity throughout the whole measurement time, i.e. it has poorer castability.

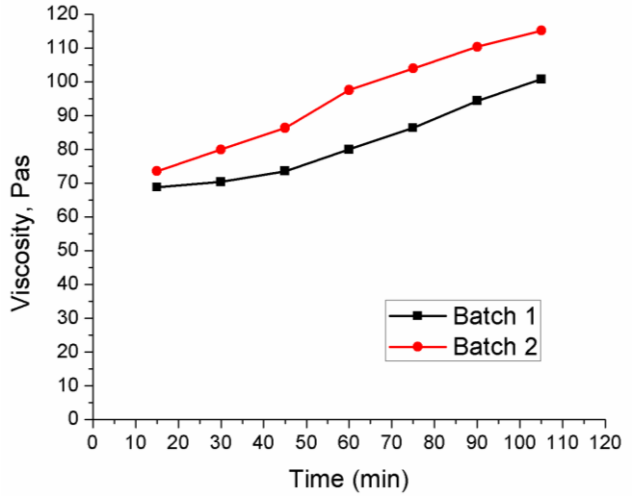

Figure 2. Viscosity-time build-up curves

3.2. Density and hardness

The results of density and hardness measurements are given in Table 3. As may be noticed, the density is higher for the samples from Batch 1. Following the fact that this batch had lower viscosities after the homogenization, it may be said that the particles of solid ingredients had better packaging, enabling higher final density.

Table 3. Densities and hardness values of the examined batches

Characteristic	Specimen	Batch 1		Batch 2	
Density ± st.dev. [g/dm^3]	1	1.662	1.667 ±0.004	1.615	1.621± 0.006
	2	1.669		1.626	
	3	1.671		1.622	
Hardness, Shore A	1	65	62.3 ±1.5	58	57.0 ±2.6
	2	62		54	
	3	60		59	

This is due to more complete plasticization of the mixture in the case when DOA was added into premix. As for the case when it was added on HMX, most probably certain amount of it stayed adhered to HMX crystals and the part of it that participated in plasticization of the mixture did not allow enough easy movement of the constituents ones along other to set down to the same density. Consequently, lower density of PBX Batch 2 has caused it`s lower hardness.

3.3. Tensile properties

The results of the tensile test for the specimens taken from PBX form both charges are shown as representative force-displacement diagrams in Figures 3 and 4 (for one of three tested specimens per batch), and as average values of maximum force (F_{max}), maximum stress (σ), strain at maximum stress (ε_{max}), strain at break (ε_{break}), and Young`s modulus of elasticity (E) in Table 4.

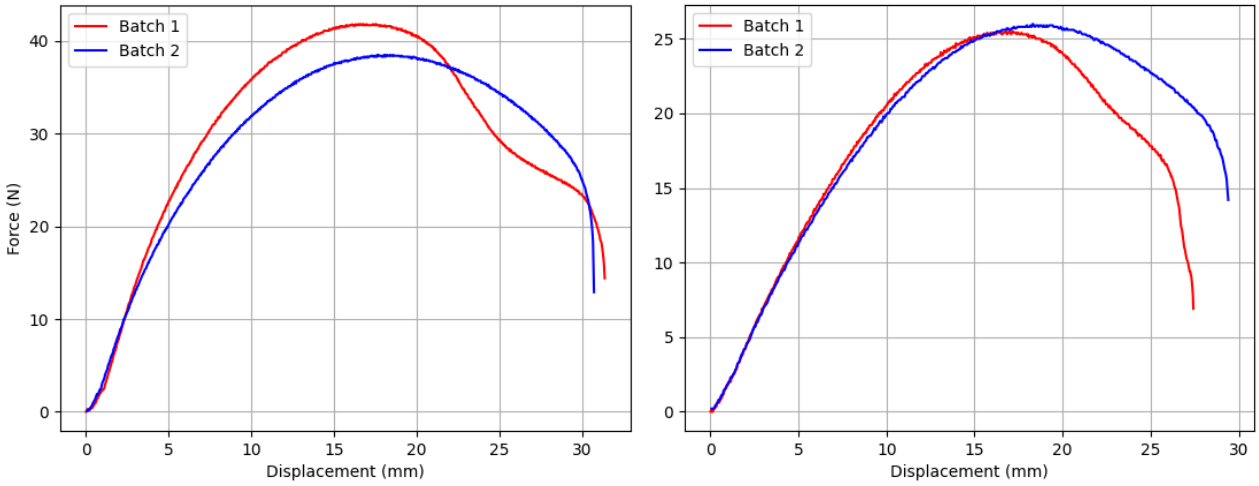

Figure 3. Force-displacement curves at -30°C (left) and at +20°C (right)

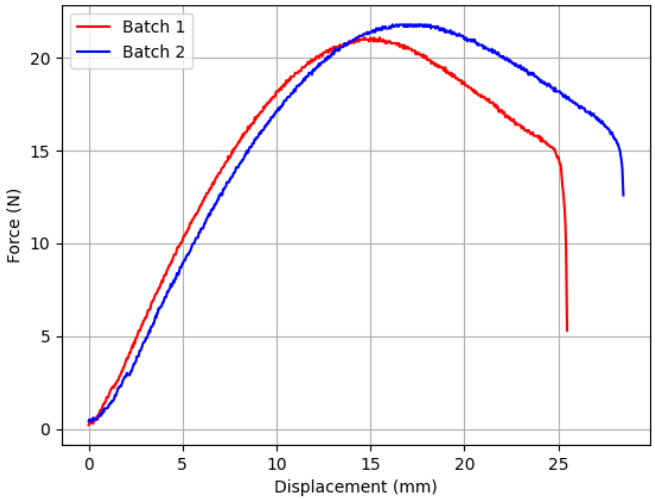

Figure 4. Force-displacement curves at +50°C

Table 4. Tensile properties of the examined batches

Temperature	*Batch*	F_{max} [N]	σ [Pa]	ε_{max} [%]	ε_{break} [%]	E [MPa]
-30°C	Batch 1	42.80	576	15.85	36.02	8.87
	Batch 2	40.23	542	17.46	30.13	7.68
+20°C	Batch 1	25.27	342	12.85	34.83	3.73
	Batch 2	26.10	348	17.81	28.34	3.47
+50°C	Batch 1	21.33	286	14.48	27.60	3.10
	Batch 2	21.57	288	15.68	24.63	2.93

The observed curves of force-displacement and the results obtained for the examined samples have revealed that the batch with DOA incorporated along with HMX had similar tensile properties at positive temperatures: it had approximately the same tensile strengths and bigger values of the elongation % at maximum force points for all the three temperatures. However, the batch with DOA

added on the beginning of the homogenization, in premix, had better strength resistance at the temperature below zero, and higher modules of elasticity at all the temperatures at which the test was conducted. Regarding the PBX, these differences are not considered to be very big, hence not very significant. But in case of rocket propellants, these differences might have much of an impact. Having in mind that PBX is actually a composite with elastomeric polymer matrix and a high content of solid fillers, it might be said that it is unusual for such a polymer composite to have better tensile properties at negative temperatures. However, here both batches have better tensile strength and modulus of elasticity at -30°C than at +20°C or +50°C, similar as in case of solid rocket propellants based on HTPB binder reported in literature [8].

4. Conclusions

The impact of the technology of incorporating dioctyl adipate as a plasticizer into a selected formulation of cast composite PBX explosive was analyzed. A batch was made with DOA added in the premix of HTPB binder and another batch with DOA added together with HMX. Comparative tests were conducted: time dependence of apparent viscosity was observed, tensile strength, density and hardness were measured. In all the time points in which the apparent viscosity was measured, it`s values were higher for the batch with DOA introduced along with HMX. Density and hardness of PBX were both higher in the case of PBX batch with DOA incorporated in the beginning of the homogenization, in the premix. Tensile properties at the room temperature and at +50°C are very similar, but at -30°C the observed batches had significantly higher tensile strength and modulus of elasticity. Differences that have been observed in the rheological and physical-mechanical properties of the PBX samples from two batches clearly indicate that the method of plasticizer`s incorporation in the mixture can affect the processability of these explosive formulations and their further applicability.

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