Influence of Differently Cured Polymeric Binders on Rheology Properties of Plastic Explosives

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Plastic Explosive Compositions consisting of HMX and liquid polyurethane binder were prepared in order to determine influence of differently cured polymeric binders on rheological properties of plastic explosives. First, a set of polymeric binders was prepared in polyaddition reaction between HTPB and IPDI, with varying NCO:OH ratio and examined through the standard and non-standard rheological tests on a dynamic rotational rheometer. Viscosity curves of polymeric binders show viscosity increase with NCO:OH ratio increase, as expected. Amplitude sweep tests reveal liquid-like structure of PEs, with structure strength increase with higher NCO:OH ratio of polymeric binder used, and limiting values of LVER vary from 10^{-3} to 10^{-2} strain. Results of creep test reveal that with increase of NCO:OH ratio of polymeric binder in PE zero-shear viscosity increase and viscous portion deformation decrease. Also, penetration decrease with increase of NCO:OH ratio. The obtained results indicate that initial rheology testing is crucial in plastic explosive formulation regarding their processability and physical properties.

Key words: **plastic explosive, polymer binder, rheology, creep.**

Introduction

PLASTIC explosives (hereinafter referred to as PE) are dispersions of crystalline explosives in polymer binders, with high content of explosive components. As a rule, polymer binders are in a liquid state. Thanks to the composition and characteristics of PE, after the action of force (shaping), they keep their shape. The mass fraction of the explosive component in PE is usually in the range of 70 wt.% to 90 wt.%. The binder gives the explosive mixture plastic properties, and at the same time phlegmatizes it (reduces the sensitivity of PE to the effect of unwanted external impulses). This type of explosive, due to its plastic behavior, is easily shaped in a wide range of temperatures, and is used above all for various types of engineering and sabotage demolitions (e.g. bridges, docks and railway tracks), is used in specific weapons such as reactive armor, and somewhat less often for the ammunition filling (such as booster charges, hand grenades, anti-tank and anti-personnel mines, anti-tank and anti-aircraft missiles) [1, 2]. The convenience of manual shaping is reflected in the fact that it is possible to quickly place various forms of PE on structures to be demolished, which can be located both on land and in water. In addition to the two mandatory, already mentioned components, various additives are added to PE compositions that modify detonation or physical properties (oxides, metal powders, antioxidants, bonding agents, plasticizers, etc.).

PEs have a high detonation velocity, a high destructive power, and at the same time a low sensitivity to external impulses, which makes them safer to handle than some other explosive compositions and charges. If necessary, by increasing the content of the inert component and adding appropriate additives, PE compositions with low detonation velocities can be obtained, for specific use.

Given that PEs are primarily used in demolition and engineering actions, it is necessary that they possess appropriate physical characteristics in terms of plasticity, consistency, stickiness, etc. The science of rheology deals with examining those characteristics, which studies the behavior of matter under the influence of force [3]. In previous research in the field of PE in Military Technical Institute, the rheological characteristics of PE were, in the absence of appropriate equipment and testing methods, examined by very indirect and subjective methods. Thus, the consistency was determined by the "Bofors" method, which involves the assessment of manual shaping, retention of plasticity and retention of the original shape after PE has been standing for some time in a climate chamber at a certain temperature and air humidity [4]. Adhesion was determined by manual molding and assessment of PE adhesion to hands during molding [5]. Also, the old method for determining penetration is outdated nowadays. For the reasons mentioned above, and with the aim of following up current achievements in research in the field of PE, it is important to consider new methods for the adequate rheological characterization of PE and binders used for the production of plastic explosives. Establishing proper methodology would be significant from the aspect of standardizing the testing of the rheological characteristics of PE, and the data obtained by testing different compositions of PE could be compared, and it could be unequivocally determined which of the mentioned compositions shows better consistency, greater stickiness and stability, etc.

As, by research in the field of PE from 2018 [6], liquid polyurethane binders obtained by the polyaddition reaction between hydroxyl-terminated poly(butadiene) prepolymer and isophorone diisocyanate crosslinker proved to be suitable for the production of PE, in this research the binders were also used based on those raw materials. Therefore, in order to gain methods for the rheological characterization of PE, four liquid polyurethane binders with different NCO:OH ratios were prepared from hydroxyl-terminated poly(butadiene) and isophorone diisocyanate. On the basis of these binders and the crystal explosive octogen, four PEs consisting of 85 wt. % of explosives and 15 wt. % binder were prepared. Due to the different NCO:OH ratio of the binder, the rheological characteristics of PE are different, and by examining these characteristics, the influence of differently cross-linked binder on the rheological characteristics of PE was observed. In this way, an insight into the validity of the applied rheological tests for testing PE was obtained. The rheological characterization of the produced binders and PE was performed on an Anton Paar rheometer MCR 302, and included [7]:

1. determination of the binder viscosity curve,

2. determination of the dependence of the dynamic rheological parameters of the binder and PE on the deformation amplitude,

3. determination of frequency dependences of dynamic rheological parameters of binder and PE,

4. PE creep test outside the linear viscoelasticity area, and

5. determining the penetration resistance and adhesiveness (stickiness) of explosives.

Materials and methods

Composition and production of binders for plastic explosives

As already mentioned in the introduction of this paper, the basic components of the binder are the prepolymer of hydroxyl-terminated poly(butadiene) and the isophorone diisocyanate crosslinker. In addition to this, the binders also contained the bonding agent triethylenetetramine and an antioxidant, N-phenyl-2-naphthylamine. The produced binders differ only in the NCO:OH ratio. The compositions of the binders are shown in Table 1. The binders are named PUPE (PolyUrethane for Plastic Explosive).

Table 1. Compositions of the binders

Binder label	NCO:OH	HTPB	IPDI	TETA	FβNA
		wt.%			
PUPE 1	0.2	96.00	1.60	0.48	1.92
PUPE 2	0.25	95.62	1.99	0.48	1.91
PUPE 3	0.3	95.24	2.38	0.48	1.90
PUPE 4	0.35	94.86	2.77	0.47	1.90

The used hydroxyl-terminated poly(butadiene) (HTPB, Shanghai Rongau Enterprises) was provided by the company TRAYAL, Kruševac. The used isophorone diisocyanate (IPDI, Merck) is a mixture of cis and trans isomers, and has a purity greater than 99%; the triethylenetetramine (TETA, Sigma Aldrich) was of technical purity (60%), and the N-phenyl-2-naphthylamine (FβNA, Sigma Aldrich) had 97% purity. The binders were made in a vertical mixer DRAIS FH. The components HTPB, TETA and FβNA were homogenized for 5 minutes at atmospheric pressure and 30 minutes under vacuum at a temperature of 60°C. Then the IPDI was added and the mixture was mixed for 5 minutes at atmospheric pressure and 15 minutes under vacuum at the same temperature. The binders were poured into glass cups and left to crosslink for 96 hours at a temperature of 70°C.

Composition and production of plastic explosives

Plastic explosives were made from manufactured binders and octogen, HMX (class 1) purchased from the factory "Prva Iskra-Namenska" Barič. Each plastic explosive was made from 15 wt. % binder and 85 wt. % of octogen in a horizontal kneader, according to the established technological procedure [8]. Plastic explosives were named PE with suffixes from 1 to 4, depending on the binder used for their production (PE 1 from binder PUPE 1, etc.).

Rheological testing

All rheological tests were performed on a rheometer MCR 302 manufactured by Anton Paar (Fig.1).

Figure 1. Rheometer MCR 302, PE adhesion and penetration resistance test

Viscosity testing

The viscosity of the produced binders and the HTPB used for the production of the binder was tested by rotary tests using a cone-plate tool. The cone with a diameter of 25 mm and an angle of 1o was the moving part, and the plate with a diameter of 50 mm was stationary. Measurements were made at a temperature of 25±0.5 °C. The shear rate was varied from 0.1 to 100 1/s (in order to obtain a value of zero viscosity and to simulate the technological process of kneading during which shear rates from 1 to 100 1/s occur) through 19 values equidistant on a logarithmic scale. In order to establish a laminar flow of the sample before reading the stress value, the length of the point measurements was also changed logarithmically from 60 s (how long the first point was measured at the lowest shear rate) to 10 s (how long the last point was measured at the highest shear rate). The distance between the tools was determined by the geometry of the tool and was 0.051 mm.

Examination of the dependence of the dynamic rheological parameters of binders and explosives on the amplitude of deformation

The dependence of the dynamic rheological parameters of binders, HTPB and explosives on the amplitude of deformation was examined using plate tools (upper movable plate with a diameter of 25 mm, lower stationary plate with a diameter of 50 mm), at a constant angular frequency of 10 rad/s and temperature of 25 ± 0.5 °C. After placement and removal of excess sample, and prior to testing, the samples were allowed to "recover" from the stresses applied during placement for 180 s. When testing the binder and HTPB, the deformation amplitude was varied from 10% to 1000% through 21 equidistant values on a logarithmic scale (10 points per decade), and the distance between the tools was 0.5 mm. When testing plastic explosives, the deformation amplitude was varied from 0.001% to 1% through 31 equidistant values on a logarithmic scale (also 10 points per decade), and the distance between the tools was 3 mm (to avoid the influence of large octogen particles on the measurement).

Examination of frequency dependences of dynamic rheological properties of binders and explosives

Frequency dependences of dynamic rheological properties of binders, HTPB and explosives under shear load in the area of linear viscoelasticity were examined to dependence on amplitude of deformation, at a temperature of 25 ± 0.5 °C. When testing the binder and HTPB, the angular frequency was varied from 628 rad/s to 1 rad/s through 28 equidistant values on a logarithmic scale (10 points per decade), the distance between the tools was 0.5 mm, and the measurement length of the points was left to the device. During the PE test, the angular frequency was varied from 10 rad/s to 0.01 rad/s through 31 equidistant values on a logarithmic scale, the distance between the tools was 3 mm, and the measurement length of the points was increased logarithmically from 20 s (how long the first point was measured at the highest angular frequency) to 100 s (how long the last point was measured at the lowest angular frequency).

PE creep test outside the linear viscoelasticity region

The creep of PE outside the area of linear viscoelasticity was tested using tools used to determine the dependence of rheological parameters, at a temperature of 25 ± 0.5°C. The samples were handled as in the the previously explained tests. The distance between the tools was 3 mm. A total of 67 points were read (the length of the point measurement was logarithmically increased from 0.1 s to 10 s) and in the recovery period 136 points (the length of the point measurement was also logarithmically increased from 0.1 s to 10 s).

Determination of penetration and adhesiveness of explosives

Determination of penetration resistance and adhesiveness of PE was performed at a temperature of 25 ± 0.5 °C, using the upper parallel plate with a diameter of 4 mm and a metal container with a diameter of 55 mm and a height of 35 mm. The mass of PE in the amount of 100 g was inserted into the container and leveled so that the height of PE in the container was about 28 mm, and the container was placed on the lower tool of the device (the lower stationary parallel plate with a diameter of 50 mm). The measurement consisted of 3 intervals, in each interval the head of the device (and thus the upper tool) moved at a constant set speed of 100 μm/s, only the direction of movement was changed. In the first interval, the direction was towards the sample (penetration interval) from the initial height of 20 mm to the final height of 10 mm. Then the direction was from sample (debonding interval), from a height of 10 mm to a height of 20 mm. The third interval was the same as the first (re-penetration). Each interval lasted 100 s, and during each interval 1000 normal force values were read.

Results and discussions

Viscosity of the binders

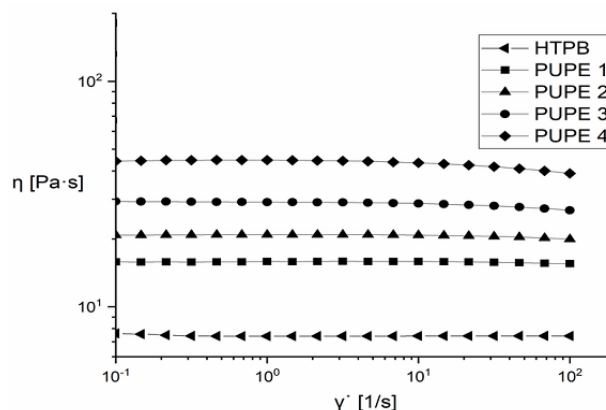Fig.2 shows viscosity curves for HTPB and the prepared binders.

Figure 2. Viscosity curves for HTPB and binders

By analyzing the viscosity curves, it can be seen that HTPB and binders with a lower NCO:OH ratio behave almost like Newtonian fluids in the range of shear rates from 0.1 to 100 1/s, i.e. that pseudoplastic behavior becomes more pronounced with increasing NCO:OH ratio. This is in line with expectations, given that with an increase in the NCO:OH ratio, the length of the macromolecular chains, i.e. the molar mass of the binder, also increases. Increasing the molar mass increases the viscosity and pseudoplasticity of polymer fluids.

Dependence of dynamic rheological parameters of binders and explosives on deformation amplitude

Fig.3 shows the dependence of G', G" and tanδ on γ on a graph with logarithmic scales for PUPE 4 binder, as a representative example. It can be seen that G">G', i.e. that the binder behaves like a viscoelastic liquid, and that the limit value of the deformation is about 60%. The graphs of the dependence of G', G" and tanδ on γ for all binders and HTPB look similar to this (all produced binders behave like viscoelastic liquids).
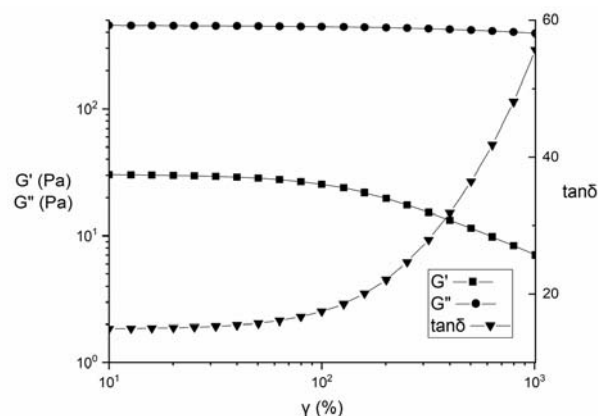

Figure 3. Graph of dependence of G', G" and tanδ on γ for PUPE 4

Fig.4 shows the dependence of G' on γ on a graph with logarithmic scales for all binders and HTPB, and it shows the above-mentioned: G' values increase with increasing NCO:OH ratio, i.e. pure HTPB has the smallest values of G' (where, conditionally speaking, the NCO:OH ratio is zero), while the binder PUPE 4, which is made with the largest amount of crosslinker, has the highest values. Also, it can be noticed that with an increase in the NCO:OH ratio, the value of G' leaves its plateau faster, i.e. that with an increase in the NCO:OH ratio, the area of linear viscoelasticity decreases. This can again be explained by the fact that with an increase in the NCO:OH ratio and an increase in the length of the polymer chains.
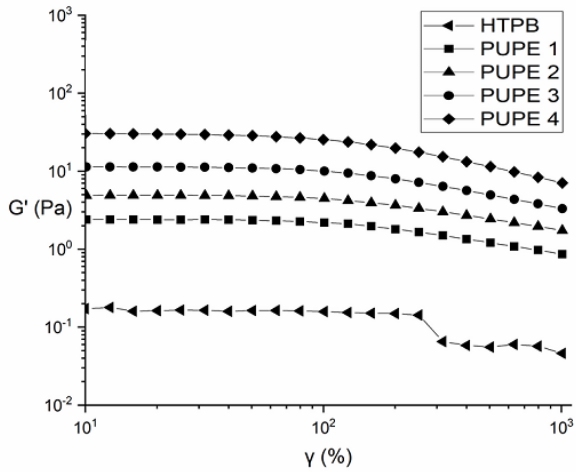

Figure 4. Graph of dependence of G' on γ for binders and HTPB

Fig.5 shows the dependence of G', G" and tanδ on γ on a graph with logarithmic scales for plastic explosive PE 4. It can be seen that G"> G', like a binder PUPE 4, PE behaves like a viscoelastic fluid. The other PE compositions also have graphs of the dependence of G', G" and tanδ on γ similar to this, that is, all PE compositions behave as viscoelastic liquids. It reveals that there are no strong forces (in this case physical forces) in the structure of plastic explosives, i.e. good interactions between the binder and the octogen crystals. This could generally be expected considering that, due to the nature of the prepolymer, the macromolecular chains of the binder are mostly non-polar and there are not many possibilities for the formation of stronger physical forces (such as dipole-dipole interactions and hydrogen bonds) between the chains and the octogen crystals.
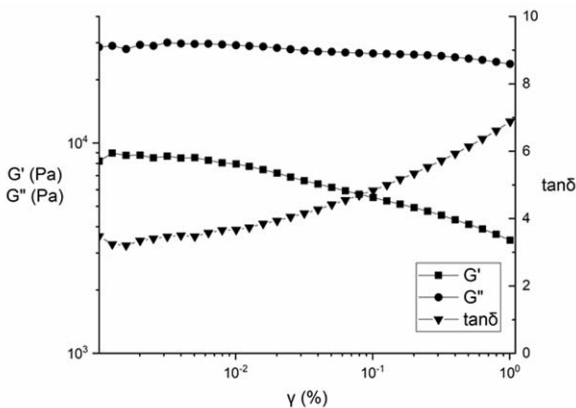

Figure 5. Graph of dependence of G', G" and tanδ on γ for PE 4

Fig.6 shows the graph of the dependence of G' for all plastic explosives. Vertical displacement is a consequence of the binder used to make PE, i.e. rigidity, because with

increasing rigidity, more energy was needed for deformation, so the modulus values are higher.
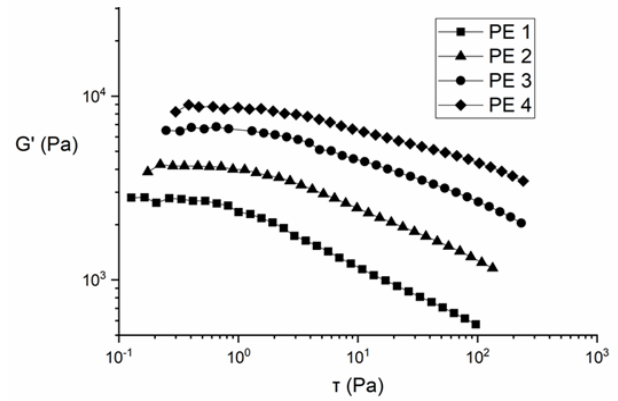

Figure 6. The dependence of G' for plastic explosives

Frequency dependence of dynamic rheological parameters of binders and explosives

Fig.7 shows the dependence of G' and G" of PUPE 1 on ω on a graph with logarithmic scales.

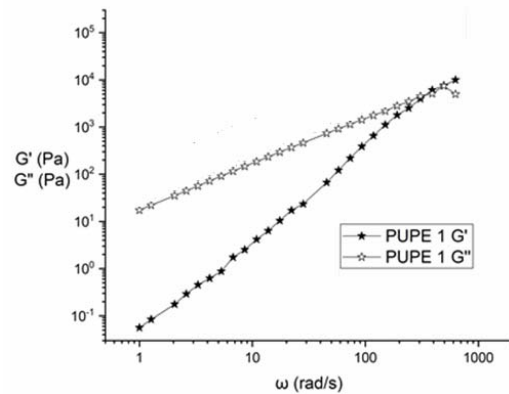**Figure 7.** G' and G" dependence on ω for PUPE 1

Due to the different molar mass of the binder, as well as differences in the chemical structure (concentration of hard segments) and interactions between macromolecular chains, the only thing that can be analyzed from the frequency dependence of the rheological quantities of the binder are the slopes of G' and G", that is, the distribution of molar masses. Table 2 shows the slope values G' and G" for HTPB and binders, obtained by linear regression of test results, as well as correlation coefficients.

Table 2. Values of slope G' and G"

	HTPB	*PUPE 1*	*PUPE 2*	*PUPE 3*	*PUPE 4*
Slope G'	1.931	1.979	1.955	1.773	1.617
Slope G"	0.998	0.962	0.954	0.926	0.896

The values of the slopes G' and G" for HTPB, PUPE 1 and PUPE 2 are very close to two and one, respectively, which means that they have a narrow molar mass distribution. In the case of other binders, with increasing NCO:OH ratio, the slope values are further away from the values of two and one, and the molar mass distributions are also wider. A wide distribution of the molar mass of the binder is not desirable, because it can be expected that during long-term standing there will be exudation of macromolecules of smaller molar masses from PE, which leads to a decrease in the binder content in PE and worse characteristics.

The frequency dependence of the dynamic rheological

parameters of plastic explosives was determined for the compositions PE 1 and PE 4, Fig.8.
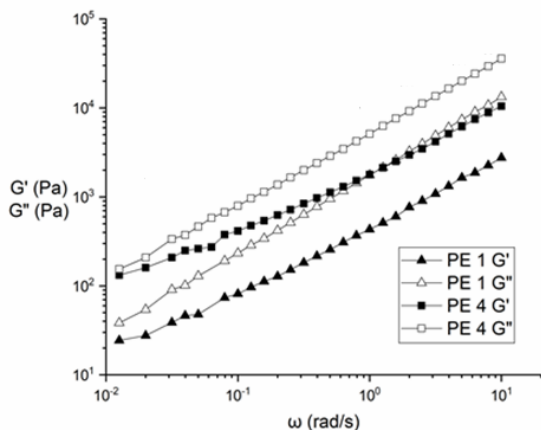

Figure 8. Graph of dependence of G' and G" of PE 1, PE 4 on ω

As can be noticed, compositions PE 1 and PE 4 at values ω→0.01 show G">G'. This means that these compositions do not have the appropriate consistency at rest, i.e. that their storage for a long period of time would cause undesirable phenomena such as phase separation and sedimentation. This can be concluded without testing for compositions PE 2 and PE 3.

Creep of plastic explosives outside the region of linear viscoelasticity

Fig.9 shows PE creep curves of the examined plastic explosives.
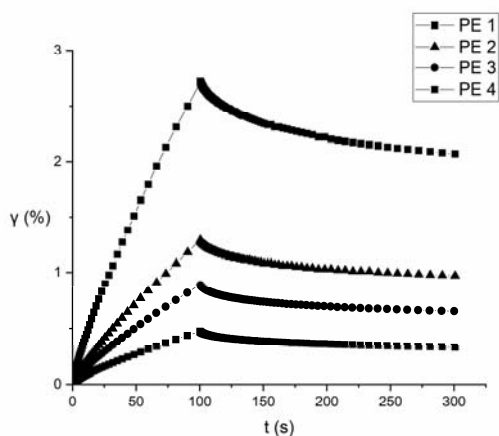
Figures 9. PE creep curves

Due to the application of the same magnitude and duration of stress in all samples, samples with a weaker structure were deformed more and those with a stronger structure less. Considering that the total deformation in all samples γ_{max} is greater than the limit value of the linear region of viscoelasticity γ_l, the basic laws of rheology cannot be applied to the obtained results. Nevertheless, the values of the return deformation γ_e and residual deformation γ_v can be analyzed. Table 3 shows those values.

Table 3. Values of total, return and residual deformation of PE

PE	γ_{max} (%)	γ_e (%)	γ_v (%)	γ_e/γ_{max} (%)
PE 1	2.720	0.650	2.070	23.89
PE 2	1.290	0.319	0.971	24.73
PE 3	0.886	0.235	0.651	26.52
PE 4	0.474	0.140	0.334	29.54

From the value of the ratio γ_e/γ_{max}, it can be concluded that the recovery of PE after the end of the force increases from the composition of PE 1 to the composition of PE 4, i.e. the elastic response rises with increasing NCO:OH ratio of the binder used to make PE.

Penetration and stickiness of plastic explosives

Table 4 shows the work values performed by the rheometer tool during PE penetration (A_{p1} work during the first penetration interval, A_{p2} work during the second penetration interval), the work values performed by the rheometer tool during PE detachment (A_o) and the ratio A_{p2}/A_{p1}. Work values are calculated using the formula

$$A = \int F(h) * dh \tag{1}$$

where h is the path traversed by the tool during penetration or detachment.

The value of A_{p1} is determined by the strength of PE, the value of A_o by the stickiness of PE, and the ratio A_{p2}/A_{p1} by the ability of PE to return to its initial state after stress, Table 4.

Table 4. Values of penetration parameters for the examined explosives

PE	A_{p1} (mJ)	A_o (mJ)	A_{p2} (mJ)	A_{p2}/A_{p1} (%)
PE 1	0.239	0.218	0.117	48.95
PE 2	0.505	0.405	0.244	48.32
PE 3	0.726	0.620	0.370	50.96
PE 4	0.945	0.771	0.483	51.11

Based on the value of Ap1, it can be concluded that the composition of PE 4 is the strongest and most adhesive. The ability of PE to return to its initial state after stress is similar for all compositions, it is slightly better for compositions PE 3 and PE 4.

Conclusions

The presented results of this research are an attempt to validly characterize plastic explosives, given the possibility that they behave non-homogeneously during rheological tests. As the test results followed the trend expected due to the different NCO:OH ratio of the binder, it can be argued that the measurements were valid.

As for the produced binders, they all behave as viscoelastic fluids, and with increasing NCO:OH ratios zero viscosity increases exponentially and the limiting value of the linear region of viscoelasticity decreases exponentially, which indicates an increase in the mean value of the molar mass by numerical representation; and that the distribution of binder molar masses is getting wider. Amplitude sweep tests of plastic explosives have shown that all plastic explosives behave like viscoelastic liquids, which means that the interaction between the binder and explosive particles is not strong, and that they do not show great consistency stability when standing.

Frequency sweeps tests of plastic explosives have shown that compositions of plastic explosives from PE 1 to PE 4 do not have a suitable consistency at rest, and would not be suitable for long-term storage.

The penetration and stickiness test showed that the PE 4 composition has the highest strength and the best stickiness, and overall it can be said that it is the best of the tested

compositions.

In further work, it is necessary to improve the binder and the composition of the plastic explosive, in order for the plastic explosive to show better rheological characteristics, primarily in order to increase the stability during rest (long-term storage).

The composition, in order to achieve better rheological characteristics, could be improved by increasing the mass fraction of explosives. Of course, then some other problems related to the production technology and possible increase in sensitivity due to the lower binder content could occur. In addition, the use of finer granulation explosives, and thus a larger specific surface area, would enhance the explosive-binder interaction.

Acknowledgement

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Uticaj različito umrežavanih polimernih veziva na reološka svojstva plastičnih eksploziva

Pripremljeni su sastavi plastičnih eksploziva koji sadrže NMH i tečno poliuretansko vezivo, kako bi se utvrdio uticaj različito umreženih polimernih veziva na reološka svojstva plastičnih eksploziva. Prvo je pripremljen set polimernih veziva u reakciji poliadicije između NTRV i IPDI, sa promenljivim odnosom NCO:OH i ispitan kroz standardne i nestandardne reološke testove na dinamičkom rotacionom reometru. Krive viskoziteta polimernih veziva pokazuju povećanje viskoziteta sa povećanjem odnosa NCO:OH, kao što se očekivalo. Test pri promenljivim amplitudama deformacije ukazuje na strukturu plastičnih eksploziva sličnu tečnosti, pri čemu se čvrstoća strukture povećava sa većim odnosom NCO:OH korišćenog polimernog veziva, a granične vrednosti LVER variraju od 10-3 do 10-2 deformacije. Rezultati testa puzanja pokazuju da se sa povećanjem odnosa NCO:OH polimernog veziva u PE povećava viskozitet nultog smicanja i smanjuje deformacija viskoznog dela. Takođe, prodor penetratora se smanjuje sa povećanjem odnosa NCO:OH. Dobijeni rezultati ukazuju da su početna reološka ispitivanja ključna u formulaciji plastičnih eksploziva u pogledu njihove preradivosti i fizičkih svojstava.

Ključne reči: **plastični eksploziv, polimerno vezivo, reologija, puzanje.**