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Effect of Inert Plasticizers on Mechanical, Thermal, and Sensitivity Properties of Polyurethane-Based Plastic Bonded Explosives

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ABSTRACT: Mechanical, thermal, and sensitivity properties of plastic bonded explosives (PBX) depend on the type of ingredients in their formulation. Aim of the work is to develop aluminized cast PBX formulations and process conditions by using alternative inert plasticizers to have similar or better properties than PBXN-109 without compromising sensitivity properties. Although very small portion of total production of plasticizers is used for solid rocket propellant and explosive formulations, they play very significant role in that area. Both inert and energetic plasticizers have involved propellant and explosive formulations to improve process parameters, mechanical properties, and even insensitivity properties of them. Isodecyl pelargonate and dioctyl adipate are the most preferred inert plasticizers in polyurethane based thermoset propellant and explosive formulations. In addition to them, diisononyl adipate and diisononyl phthalate were used and screened as inert plasticizer candidates for aluminized cast PBX formulations. Mechanical, thermal, and sensitivity properties of PBX formulations were studied and compared in detail. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40907.

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INTRODUCTION

Plasticizer is a low molecular weight additive which makes production easier for materials, hard to process by themselves because of their nature. Some of the important benefits gained by inclusion of plasticizer are given as: improved flow and flexibility, decrease in glass transition temperature, improved mechanical properties, and low temperature usage.

Phthalates and adipates are the major plasticizers used in daily life. Dioctyl phthalate, diisononyl phthalate (DINP), dioctyl adipate (DOA), and diisononyl adipate (DINA) are some of the most common plasticizers among them.

Chemical compatibility, miscibility, volatility, and glass transition temperature are the main parameters for the selection of plasticizer. First of all, a plasticizer should not react with the main polymer during production and in use.

The second crucial criterion is miscibility which is based on "like dissolves like" principle. Polarities and solubility of plasticizer and the polymer should be similar for better miscibility.¹

Migration of plasticizer is one of the main problems in plastic bonded explosives (PBX) and solid rocket propellants.^{2,3} Depending on the rate of migration, polymer loses flexibility and cannot fulfill mechanical requirements. Volatility is the main reason for migration together with the washing of by a solvent like water, alcohols, etc. Volatility is directly related with the molecular weight of the plasticizer.³

One of the advantages of plasticizer is to decrease glass transition temperature (T_g) of a polymer by creating free volume. Hereby, workability and low temperature usage of polymer is improved.

Both inert and energetic plasticizers have involved propellant and explosive formulations to improve process parameters, mechanical properties and insensitivity properties of them.^{4–7} 1,2,4-Butanetriol trinitrate, trimethylolethane trinitrate, nitroglycerin, *n*-butyl-2-nitratoethyl-nitramine, triethyleneglycol dinitrate, and bis(2,2-dinitropropyl)acetal or formal are energetic plasticizers used in especially smokeless or reduce smoke propellant formulations to compensate energy loss due to reduction or removal of metallic fuel which is responsible for primary smoke generation.

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Properties	DOA	IDP	DINA	DINP
Mwt	370.6	298.5	398	418
Density (g/cm ³)	0.927	0.867	0.950	0.975
Viscosity (cP)	22 @25°C	4.2 @40°C	18-22 @20°C	68-82 @20°C
Pour point (°C)	-75	-72	-68	-45
Flash point (°C)	>190	172	>204	>210

Table I. Properties of Plasticizers¹²⁻¹⁸

Effect of ingredients on mechanical and physical properties of polyurethane based energetic composites (propellants and explosives) was studied in many aspects before. It has been shown that type, amount, ratio, and particle size of ingredients have substantial effects on mechanical and physical properties of them.^{8–10} Aim of this study is to develop aluminized polyurethane based PBX formulations and process conditions by using alternative inert plasticizers to have similar or better properties than PBXN-109 without compromising insensitivity properties. Isodecyl pelargonate (IDP) and DOA are the most preferred inert plasticizers in polyurethane based thermoset propellant and explosive formulations. In addition to them, DINA and DINP were chosen and screened as inert plasticizer candidates. Those plasticizers were proposed as alternative plasticizer for PBX formulation very recently by United States Patent number 8,172,965¹¹.

EXPERIMENTAL

Chemicals

The binder used for PBX preparation was military grade hydroxyl-terminated polybutadiene (HTPB R45M), with 1 wt % 2,2'-methylenebis (4-methyl-6-tertbutylphenol) (AO-2246), was supplied from Cray Valley Company, USA. DOA, DINA, and DINP were the plasticizers used in PBX formulation were commercial product of Plastifay Kimya, Istanbul. The other plasticizer IDP was production of Cognis Corporation. Some of the properties of inert plasticizers either provided by the supplier or from the referred literature are shown in Table I. Chemical structures can be given as Supporting Information.

Isophorone diisocyanate was used as a curing agent and supplied from Bayer Material Science. Reduced sensitivity cyclotrimethylene trinitramine (RS-RDX) was used as an energetic filler and provided by Chemring Nobel with two different particle sizes, Class 1 and Class 5 as defined by MIL-DTL-398D "Detail Specification RDX".¹⁹ di–(2–hydroxyethyl)–5, 5-dimethylhydantoin (DHE or Dantocol DHE) was supplied from Lonza. Ferric acetylacetonate (FeAA) with > 99.9 purity was supplied from Aldrich. 2,2′-Methylenebis (4-methyl-6-tertbutylphenol) AO-2246 also known as Vulkanox BKF was provided by Rhein Chemie Germany. Type IV spherical aluminum powder was supplied from Toyal America, according to MIL-PRF-23950B (AS) "Performance Specification Aluminum Powder, Spherical." All chemicals were used as received in formulation studies.

Instruments and Analysis

Quantachrome Manuel Gas Stereopycnometer (Model: SPY-3) with 135 cm³ (5 cm diameter \times 7.5 cm length) stainless steel sample cell was used for density measurement. Approximately

60-90 g samples were measured at room temperature in Helium atmosphere and average of five measurements were reported.

Viscosity measurements of uncured explosive were done by using HBDV-II Brookfield Digital Viscometer at 50°C and with T-B type T-bar spindle. Uncured explosive has paste type behavior that cause cavities during viscosity measurement. Helipath stand was used to solve that problem. That stand raise and lower the spindle to create a helical movement and prevent cavity formation (channeling effect). Pot life and end of mix viscosity (EOMV) measurements were done by one rpm rotational speed. Additional to EOMV measurements, viscosities of explosives with different rotational speeds (2, 3, 5, 7, 10 rpm) were measured and reported as well. All viscosity measurements were done by using 500 mL uncured explosive samples.

Uniaxial tensile tests were done at room temperature by using Chatillon LTCM-100 instrument and Chatillon 100 LBF (445 N) AMETEK load cell. All tensile measurements for explosives were done with 50 mm/min testing speed as described in STA-NAG 4506.²⁰

Autoignition temperatures of explosives were measured according to STANAG 4491 "Explosives, Thermal Sensitiveness and Explosiveness Tests, Annex B-1: Temperature of Ignition" by a test set up designed and produced in Turkey.²¹

LINSEIS L75 Vertical Bench Top Platinum Series dilatometer with 100 mN force gauge was used to measure glass transition temperatures (T_g) of explosives with 6 mm diameter and 5.69 ± 0.07 mm length samples. First, samples were cooled down to -110° C by 2°C/min cooling rate, then waited for stabilized temperature and heated to -20° C by 2°C/min heating rate.

Decomposition temperature determination of explosive samples was performed by Mettler-Toledo TGA/DSC 1 thermogravimetric analyzer. A total of 50 mL/min nitrogen gas was flowed over 3-5 mg samples in a 70 μ L platinum pan. First, samples were flashed for 10 min under nitrogen gas at 30°C. Then, 5°C/min heating rate was applied to attain 550°C.

C-Therm Tci Thermal Conductivity Analyzer was used to measure thermal conductivity of explosive samples ($25 \times 25 \times 12$) ± 2 mm in dimensions.

Impact sensitivity of explosives was tested by BAM impact machine according to STANAG 4489 "Explosives, Impact Sensitivity Tests, Annex C: BAM Impact Machine."²² Solid samples with $3 \times 4 \times 4$ mm dimensions and 10 mm³ powder samples with particle size between 1.0 and 0.5 mm mesh screen were



Table II. Explosive Codes Containing Different Plasticizers

Plasticizer type	DOA	IDP	DINA	DINP
Explosive code	P-1	P-2	P-3	P-4

tested. Bruceton up and down procedure was used to obtain 50% probability of reaction.

Friction sensitivity tests were done by BAM friction method according to STANAG 4487 "Explosives, Friction Sensitivity Tests, Annex A: BAM Friction Machine."²³ Approximately 10 mm³ of the material, maximum 1 mm thick by 5 mm in diameter, were used as solid samples. Powdered substances were sieved through a 0.5 mm mesh screen. A measuring spoon fabricated out of conductive plastic was used to measure 10 mm³ of powder.

Electrostatic discharge tests were done by using ESD 2008 "A small-scale electrostatic spark sensitivity tester" which is developed by OZM research s.r.o in cooperation with "Institute of Energetic Materials," University of Pardubice, according to AOP 7 "Manual of Data Requirements and tests for The Qualification of Explosive Materials for Military Use" and the manual written by that company.^{24,25} Samples less than 10 mg were tested at relative humidity <50% and at room temperature.

Hardness measurements were performed by Bareiss Shore-A Durometer according to MIL-E-82886(OS) "Military Specification, Explosive, Plastic Bonded, Cast PBXN-109."²⁶ After 10 days of curing process, explosive blocks were sliced into 6–7 layers, upper and lower levels were discarded and hardness data was taken from the rest of the layers after 24 h conditioning at room temperature. In each test, after 30 s values were recorded for appropriate measurement.

STABIL Vacuum Stability Tester made by OZM Research Company was used to survey compatibility of ingredients, as described in MIL-E-82886(OS).²⁶ All samples were tested in the calibrated test tubes at 100°C for 48 h.

FEI Quanta 400F model Scanning Electron Microscope was used for surface analysis of explosives. Explosive samples were inserted in liquid nitrogen, and then broken at their midpoint and plated 7 nm with Au-Pd by sputter method before analysis. SEM analysis was done under low vacuum (0.8 mbar) and 10 kV was applied from 10.8 to 13.4 mm distance. Field emission gun was used during analysis. Photos of those tests can be given as Supporting Information.

Explosive Preparation

After optimization of formulation and process parameters, four batches of explosive production were done by using one US galloon vertical planetary mixer with four different types of plasticizer. The explosive formulations were given codes to distinguish them as shown in Table II. Explosive mixtures were produced at 50°C according to typical explosive preparation procedure with the ingredients given in Table III. Right after the mixing process, EOMV and pot life measurements were done. Other measurements were performed after 10 days of

Table III. Plastic Bonded Explosive Ingredients

Ingredients	Percentage (wt %)
RS-RDX II Class 1	58.18
RS-RDX II Class 5	5.82
Aluminum powder, spherical, Type IV	20.00
HTPB R45M (with 1.0% AO 2246)	7.47
Isophorone diisocyanate	0.93
Ferric acetyl acetonate	0.0008
Plasticizer	7.33
di-(2-hydroxyethyl)-5, 5-dimethylhydantoin	0.27

curing process at 50°C to ensure complete curing of the explosive. FeAA was used as catalyzer to accelerate curing. Curing process was followed by mechanical, thermal, and sensitivity characterization of explosives.

RESULTS AND DISCUSSION

Compatibility of the ingredients was the first issue that should be carried out before formulation studies. Reactions arising from incompatibility have significant effect on shelf life of explosives. Incompatibility reactions between plasticizer and other main ingredients (binder, energetic filler, and metal powder) of explosive can further accelerate the rate of ageing. Compatibility of an explosive is the primary issue and has to be entirely investigated for every step.²⁷

Therefore, compatibility is one of the important criteria for convenient plasticizer in PBX formulation. Vacuum stability test (VST) is the most widely used and accepted method for chemical compatibility because it is reliable and relatively short test. The amount of sample used in VST test is much more representative than the amount used in TGA or DSC method.²⁸ Higher sample size increases the possibility of physical contact in between the materials tested, and ensures the reliability. On the other hand, the foremost advantages of using DSC and TGA methods are to make experiments quicker and safer.²⁹ However, TGA and DSC methods are suitable for the testing of primary explosives and pyrotechnics, their applicability for propellants, and PBX can be questioned.

VST compatibility test results of HTPB, plasticizers, RDX, and aluminum are given in Table IV. All values are found to be well below the 5 mL and even less than 0.150 mL. This proves that all plasticizers in question are compatible with the HTPB, RDX, and aluminum. VST test results less than 1 mL can also be commentated as insignificant incompatibility according to criteria put forth by a study published in 2006.³⁰ The results with

 Table IV. Compatibility of Plasticizers with Main Explosive Ingredients

 According to VST (mL gas)

Components	DOA	IDP	DINA	DINP
HTPB	-0.249	0.116	-0.021	-0.148
RDX	-0.030	-1.989	-0.100	-0.234
Al powder	-0.339	-1.836	-0.309	-0.281



	Test results			
Test name	P-1	P-2	P-3	P-4
Density (g/cm ³)	1.668	1.649	1.668	1.671
EOMV (Poise)	3845	5339	4126	2869
Pot life (min)	≥180	≥180	≥180	≥180
σ @ max. load (MPa)	0.46	0.59	0.43	0.47
Modulus (MPa)	3.01	3.31	2.72	2.76
Elongation (%)	34.5	32.18	34.95	27.70
Autoignition Temp. (°C)	224	222	224	228
T _g (°C)	-86.5	-90.0	-83.0	-81.0
Decomposition Temp. (°C)	217.1	218.6	218.3	214.6
K (W/m K)	0.81	0.71	0.80	0.84
BAM impact (J)	19.98	17.27	17.89	16.34
BAM friction (N)	≥360	>360	>360	>360
ESD (mJ)	117	114	119	116
Hardness (Shore A)	44	49	41	42
VST (mL gas/g)	0.279	0.142	0.163	0.138

 Table V. Characterization Results of Explosives (Explosive Codes are Shown in Table II)

minus sign are also indication of compatibility and reported in many studies.^{28,30,31}

After compatibility, formulation, and process optimization studies, four different explosive formulations were prepared each containing different type of plasticizer. Explosive productions were done by using the same production parameters and recipe except plasticizer. Characterization results of rheological, mechanical, thermal, and sensitivity properties of uncured and cured explosives were summarized in Table V.

Average of five consecutive results showed that there is a direct relationship between density of individual plasticizers and explosive formulations including those plasticizers. All of the explosive formulations exceedingly meet the requirements (30 Shore-A) given in military standard (MIL-E-82886).

Pot life is described as the elapsed time until the viscosity of explosive is still convenient for casting process.³² Accepted upper viscosity limit for propellants and explosives is around 20 kP for proper casting. Casting process can be done by several methods. If viscosity of explosive is low enough (\leq 3000 poise), only vacuum applied to the casting volume could be sufficient for proper casting. If viscosity of explosive is high, pressure casting technique accompanying vibration is one of the methods studied for highly loaded propellants.³³

Explosive viscosities less than 10 kP are accepted successful after 3 h lapsed from the mixing. Ranking of explosives containing different type of plasticizer according to the EOMV measurements were as follows: P-4 < P-1 < P-3 < P-2. Difference in EOMV values can only be explained by the type of plasticizer. It was interesting to note that explosives containing adipate type plasticizers (P-1: DOA, P-3: DINA) have small difference in EOMV, but DINA has totally two more $-CH_2$ — group in its carbon chain.



Figure 1. Variation of viscosity versus rpm of the explosive compositions (symbols are shown in Table II).

While explosive containing IDP plasticizer (P-2) has highest EOMV, explosive containing DINP (P-4) has the lowest. DINP has aromatic ring in its structure and occupy more volume than the other plasticizers. On the other hand, IDP has very long linear aliphatic chain in its structure. It is expected that molecules with aromatic rings and branched chains create more free volume than linear chains and lower viscosity of the mixture more than the linear ones.³⁴ EOMV results are lower than the viscosities measured in similar studies in the literature. EOMV of PBXN-109 including insensitive RDX from Dyno Nobel and DOA plasticizer has been measured as 6000 Poise which is 56% higher than the results obtained in this study.³⁵

The viscosity (η) defined as the ratio of shear stress (τ) to shear rate (γ) . Uncured PBX show non-Newtonian (time independent, shear dependent) flow behavior and generally power law model is used to define them as shown in eq. (1).

$$\eta \equiv \frac{\tau}{\gamma} = \frac{K\gamma^n}{\gamma} = \mathbf{K}\gamma^{n-1} \tag{1}$$

where n = 1, n < 1, and n > 1 represents Newtonian, pseudoplastic, and dilatant flows, respectively.

Viscosities of explosives were measured at 6–7 different viscometer speeds and results are shown in Figure 1. Results of viscosity measurement proved that the flow behavior depends on shear rate which is a linear function of viscometer speed (rpm).

For a power law, fluid log-log plot of viscosity versus rpm is always linear as shown in Figure 2. Good linearity on slopes proves that data is well fitted with the power law.^{36,37} Slope is



Figure 2. Log-log viscosity versus rpm for explosives (symbols are shown in Table II).

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Table VI. K and n Values of Explosives (Explosive Codes are Shown in Table II)

	P-1	P-2	P-3	P-4
К	4024	5950	4254	2948
n	0.5262	0.3914	0.5263	0.6113

equal to flow behavior index (measure of deviation from Newtonian behavior) minus one (n-1) and intercept refers to log of consistency coefficient (K).

In our case, uncured explosive shows pseudoplastic behavior. K and *n* values calculated from the equations obtained from Figure 2 are shown in Table VI.

Degree of pseudoplasticity can be measured by flow behavior index. As n increases pseudoplasticity decreases so IDP containing explosive (P-2) shows high pseudoplasticity among others. Flow behavior index of two adipate plasticizer containing explosives (P-1 and P-3) are almost the same. All four explosive formulations containing different plasticizers achieved 3 h pot life requirement with less than 6 kP viscosity which ensures enough time for the filling process.

Filler size, filler geometry, and adhesion between filler and the polymer are some of the factors that affect the final mechanical properties. It was argued that sharp edges of standard RDX crystals may act as stress concentrators causing a reduction in strain at maximum load.³⁸ Both improved RDX and RS-RDX from Chemring Nobel Company has better roundness than standard Type II RDX. Aluminum powder used in all formulations has also spherical shape. It is also known that shape of the fillers have important role on elastic or tensile modulus of composites. Modulus is increasing with the aspect ratio of the fillers. Short fibers are the most appropriate choice for better tensile properties. Flakes and irregular shaped particles also improve mechanical strength of composites more than spherical ones. Spherical inert and energetic filers are the most prominent reason for low tensile modulus of explosives with RS-RDX.

Explosive containing IDP (P-2) plasticizer has superior tensile

chain of IDP cause higher mobility, and thus provide better stress transfer.

DINP and DOA show similar mechanical behavior in explosive formulations. DINP is the only plasticizer candidate with aromatic ring in the structure. Although it has the highest molecular weight among other plasticizers, because of its bulky structure, it creates higher free volume than others. That would be the explanation for having lower Young's modulus.

Explosives in the munitions are exposed either mechanical and thermal stresses or shocks during their transportation, usage, and storage. Therewithal, aging is another mechanism which lowers the mechanical properties by the time. Higher elongation and stress values are critical to resist that kind of conditions. If mechanical properties of explosives are not sufficient to compensate these stresses, some cracks may occur in the explosives. Cracks in the explosive promote an increase in sensitivity of the munition. All of the explosives containing different type of plasticizers show excellent mechanical properties and fulfill all mechanical requirements defined by military standard.²⁶

Glass transition temperature was calculated from the first derivative of elongation versus temperature graph in dilatometer. T_{σ} values of explosives can be put in order as follows: P-2 < P-1 < P-3 < P-4. Viscosity data of plasticizers in corresponding explosive formulations are in the same order with explosives: IDP < DOA < DINA < DINP as expected. According to the results obtained, all explosive formulations are suitable for military applications where -54°C is the minimum temperature at which munitions could be used or stored. Dilatometer curve of explosive sample with DOA plasticizer can be given as Supporting Information.

Direct relationship between density and thermal conductivity is one of the well-known basic principles. One may easily conclude that thermal conductivity of explosives is increasing with an increase in explosive densities as shown in Figure 3.

Peak decomposition temperatures of all explosive formulations were around 215-219°C as shown in Figure 4. TGA results show that plasticizer type has no significant effect on decomposition temperature of the explosives.



properties among other explosives containing different plasticizers. In fact, linear structure, low molecular weight, and long

Upper limit for compatibility of PBXN-109 at 100°C for 48 h is 0.5 mL per 1 g sample. All compositions were under this limit and therefore can be accepted as stable.



Figure 3. Thermal conductivity (○) and density (■) relationship (symbols are shown in Table II).

Figure 4. Decomposition temperatures of explosives (symbols are shown in Table II).



Figure 5. SEM image of explosive containing DOA as a plasticizer.

Average of four measurements was taken as the autoignition temperature. Explosive with DINP plasticizer shows slightly higher autoignition temperature than the other compositions. That could be explained by higher thermal resistance of DINP among other alternative plasticizers. Test results are consistent with the PBXN-109 measurements done by Australian "Defence Science and Technology Organization."^{38–40}

Impact sensitivity results are given in terms of Joule. Uncoated regular RDX impact sensitivity result was reported as 6.85 J in the literature which is less than 9.80 J measured for RS-RDX in this study as expected.⁴¹ While RS-RDX without any coating has 9.80 J impact sensitivity, after coating with polyurethane matrix almost 100% improvement (16.3–20.0 J) was gained in impact sensitivity value. Similar amount of impact insensitivity improvements for different kind of RDX were reported in the



Figure 6. SEM image of explosive containing IDP as a plasticizer.



Figure 7. SEM image of explosive containing DINA as a plasticizer.

literature after forming PBXN-109 compositions.³⁸ While all explosives containing different kind of plasticizer have positive contribution to insensitivity of RDX, explosive containing DOA as plasticizer (P-1) somewhat had higher influence. Although 2.0–3.5 J difference in impact sensitivity corresponds to 10–20% higher insensitivity and cannot be ignored, all explosives containing different kind of plasticizer provide better insensitivity than virgin RDX.

While friction sensitivity of RS-RDX by itself was 156 N, after coating with polymer matrix, there was a significant increase in insensitivity. Ratio of sensitivity values before and after the coating process reported in several studies.^{35,38–40} All explosive formulations containing different plasticizers have equal or more than 360 N friction sensitivity.

No ignition was observed from the explosive compositions subjected to ESD sensitivity test. ESD sensitivity results were pointed out an apparent unleashed odor from the explosive samples. When RDX crystals were coated by polyurethane matrix, ESD sensitivity were improved significantly. Null RDX has 55 mJ ESD sensitivity according to AOP-07 (ED-2).²⁴ There was no big difference in between the sensitivity results of explosives containing varied plasticizers.

As shown in SEM images, aluminum and RDX particles were perfectly coated by polyurethane matrix containing DOA as plasticizer (Figure 5). Cracks observed at the surface of powders was due to the heating effect of high voltage (10 kV) applied for a while on the surface of the samples during imaging.

Although surface of the P-2 explosive containing IDP plasticizer had wrinkled surface, both aluminum and RDX powders were seemed to be well coated by the polyurethane matrix (Figure 6). Formation of the holes was due to the randomly formed wrinkles and not a result of debonding behavior of solid particles.

Polymer coating on the surface of solid particles of P-3 explosive was easily seen from Figure 7. There was no evidence for





Figure 8. SEM image of explosive containing DINP as a plasticizer.

debonding. The same type of cracks on the surface has been observed as in the case of P-1 explosive. Surface of P-1 and P-3 explosives which have the same type of plasticizer (adipate) have similar appearance. Coating of aluminum and RDX particles in P-4 explosive which contains DINP as plasticizer was also successful as shown in Figure 8.

Except impact sensitivity test, all insensitivity measurements showed that four explosive samples containing different plasticizer have similar behavior against unpredictable stimuli. Coating of explosive particles has an important role on insensitivity behavior of the cured explosive mix. Together with wetting of particles by the polymer matrix, physical and chemical bonds are important factors for appropriate coating process. In order to improve interaction between solid particles and polymer matrix DHE had been used as bonding agent in the formulations. Solids having higher surface energies are most likely to be wetted by the polymer matrix. DHE increases the surface energy of RDX particles resulting with better adhesion with the polyurethane matrix. It has been proved that lower interfacial tension of binder to explosive supports easier coating and lower impact sensitivity.⁴² Relatively lower impact sensitivity of P-4 might be the indication of undesirable voids. During impact sensitivity measurement, those voids adiabatically compressed and cause sudden heat formation which is well enough to initiate a reaction like decomposition, explosion etc.

CONCLUSIONS

Two new inert plasticizer candidates as an alternative to DOA and IDP were investigated for aluminized plastic bonded cast explosives. DINA and DINP were also selected because of: relatively low molecular weight, good thermal stability, low volatility, and good flow properties at process temperatures.

Rheological, mechanical, thermal, sensitivity properties of explosives were studied in detail and following conclusions have been made:

- All plasticizers were found as compatible with HTPB, RDX, and aluminum.
- Density, hardness, tensile properties, and vacuum stability of all explosive formulations with different type of plasticizers fulfill the requirements defined in MIL-E-82886(OS).
- EOMV results show that molecules with aromatic rings and branched chains create more free volume than linear chains and lowers viscosity of the mixture.
- All alternative formulations have reasonable pot life and are suitable for mass production.
- Thermal conductivity results are parallel to density of the explosives.
- All thermal behaviors of explosives are suitable for the conditions from -54°C to +71°C.
- A sharp decrease in sensitivity of RS-RDX has been observed after coating with polymer matrix.
- New plasticizer candidates are suitable for aluminized cast polymer bonded explosives.

According to the results, it cannot be concluded that the new plasticizer candidates are superior to the former plasticizers on the basis of performance but they are acceptable. On the other hand, especially DINP may improve aging characteristics of PBXs because of its higher molecular weight, due to decrease in the migration of plasticizer. DINA and DINP were promising plasticizer alternatives not only because of their compatibility with the main explosive ingredients, but also their considerable improvement action on tensile and insensitivity properties of explosive.

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REFERENCES

- Abou-Rachid, H.; Lussier, L. S.; Ringuette, S.; Lafleur-Lambert, X., Jaidann, M.; Brisson, J. *Propell. Explos. Pyrot.* 2008, *33*, 301.
- 2. Provatas, A. Energ. Mater. 2003, 21, 237.
- 3. Gottlieb, L.; Bar, S. Propell. Explos. Pyrot. 2003, 28, 12.
- 4. Elbeih, A.; Zeman, S.; Pachman, J. Cent. Eur. J. Energ. Mater. 2013, 10, 339.
- Kumari, D.; Yamajala, K. D. B.; Singh, H.; Sanghavi, R. R.; Asthana, S. N.; Raju, K.; Banerjee S. *Propell. Explos. Pyrot.* 2013, 38, 805.
- Muthiah, R.; Somasundaran, U. I.; Verghese, T. L.; Thomas, V. A. Def. Sci. J. 1989, 39, 147.
- 7. Wingborg, N.; Eldsäter, C. Propell. Explos. Pyrot. 2002, 27, 314.
- 8. Hocaoğlu, Ö.; Özbelge, T.; Pekel, F.; Özkar S. J. Appl. Polym. Sci. 2002, 84, 2072.
- 9. Göçmez, A.; Erişken, C.; Yılmazer, Ü.; Pekel, F.; Özkar S. J. Appl. Polym. Sci. 1998, 67, 1457.



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- 10. Benli, S.; Yılmazer, Ü.; Pekel, F.; Özkar, S. J. Appl. Polym. Sci. 1998, 68, 1057.
- 11. Daoud, S.; Berger, T. R.; Villeburn, M. J. U.S. Pat. 8, 172,965 (2012).
- BASF Corporation. Di-(2-Ethylhexyl) Adipate Technical Data Sheet; BASF Corporation: USA, 2009.
- 13. Plastify Chemical Industry. Di Octyl Adipate Certificate of Analysis; Plastify Chemical Industry: İstanbul, **2003**.
- HB Chemical Corporation. Di Octyl Adipate Material Safety Data Sheet; HB Chemical Corporation: Cuyahoga Falls, 2008.
- Synlubestechnology. Isodecyl Pelargonate Technical Data Sheet (EMERY[®] 2911); Cognis Corporation: USA, 2000.
- Plastify Chemical Industry. Plast 51 Product Specifications; Plastifay Chemical Company: Turkey, 2010.
- 17. BASF. Diisononyl Adipate (Plastomoll[®] DNA) Technical Data Sheet; BASF Corporation: USA, **2009**.
- 18. Plastifay Chemical Industry. Diisononyl Phthalate Product Specification; Plastifay Chemical Industry: İstanbul, **2007**.
- 19. Defense Quality and Standardization Office. MIL-DTL-398D Detail Specification of RDX; Defense Quality and Standardization Office: Picatinny Arsenal, **1996**.
- North Atlantic Treaty Organization. Explosive Materials, Physical Mechanical Properties Uniaxial Tensile Test, STANAG 4506 (Ed-1); NATO: Belgium, 2000.
- 21. North Atlantic Treaty Organization. Explosives, Thermal Sensitiveness and Explosiveness Tests, Annex B-1 Temperature of Ignition, STANAG 4491 (Ed-1); NATO: Belgium, **2002**.
- 22. North Atlantic Treaty Organization. Explosives, Impact Sensitivity Tests, Annex C: BAM Impact Machine, STANAG 4489; NATO: Belgium, **1999**.
- 23. North Atlantic Treaty Organization. Explosives, Friction Sensitivity Tests, Annex A: BAM Friction Machine, STANAG 4487 (Ed-2); NATO: Belgium, **2009**.
- 24. North Atlantic Treaty Organization. Manual of Data Requirements and Tests for The Qualification of Explosive Materials for Military Use, AOP-07 (Ed-2); NATO: Belgium, 2003.
- 25. OZM Research s.r.o. User's Manual for Electrostatic Spark SensitivityTester ESD 2008; OZM: Czech Republic, **2009**.

- Naval Surface Warfare Center. Material Specification Explosive, Plastic-Bonded, Cast PBXN-109, MIL-E-82886(OS); US DoD: USA, 1993.
- 27. Vogelsanger, B. Chimia 2004, 58, 401.
- Krabbendam-La Haye, E. L. M.; de Klerk, W. P. C.; Miszczak, M.; Szymanowski, J. J. Therm. Anal. Calorim. 2003, 72, 931.
- 29. Mazzeu, M. A. C.; Mattos, E. d. C.; Iha, K. J. Aerosp. Technol. Manage. 2010, 2, 53.
- 30. Myburgh, A. J. Therm. Anal. Calorim. 2006, 85, 135.
- 31. de Klerk, W.; van der Meer, N.; Eerligh, R. *Thermochim.* Acta 1995, 269/270, 231.
- Daniel, M. A. DSTO-GD-0492, Technical Report; Defence Science and Technology Organisation: Edinburgh, Australia, 2006.
- 33. Dombe, G.; Jain, M.; Singh, P. P.; Radhakrishnan, K. K. Indian J. Chem. Technol. 2008, 15, 420.
- 34. Seymour, R. B.; Carraher, C. E., Jr. Structure Property Relationships in Polymers; Plenum Press: New York, **1984**; p 100.
- 35. Lundwall, N.; Bui-Dang, Q.; Hays, B.; Minnick, K. In Insensitive Munitions and Energetic Materials Technology Symposium, San Francisco, CA, USA, November 15–17, **2004**.
- Rosen, S. L. Fundemental Principles of Polymeric Materials; Wiley: USA; Canada, 1982; pp 199–207.
- Mahanta, A. K.; Goyal, M.; Pathak, D. D. Malays. Polym. J. 2010, 5, 1.
- Lochert, I. J.; Dexter, R. M.; Hamshere, B. L. DSTO-TN-0440, Technical Report; Defence Science and Technology Organisation: Edinburgh, Australia, 2002.
- 39. Hamshere, B. L.; Lochert, I. J.; Dexter, R. M. DSTO-TR-1471, Technical Report; Defence Science and Technology Organisation: Edinburgh, Australia, **2003**.
- 40. Dexter, R. M.; Hamshere, B. L.; Lochert, I. J. DSTO-TN-0441, Technical Report; Defence Science and Technology Organisation, Edinburgh, Australia, **2002**.
- An, C. W.; Guo, X. D.; Song, X. L.; Wang, Y.; Li, F. S. J. Energ. Mater. 2009, 27, 118.
- 42. Shim, J. S.; Kim, H. S.; Lee, K. D.; Kim, J. K. In AlChE Annual Meeting, Austin, TX, USA, November 7–12, 2004.

