DIPROPYLENE GLYCOL BIS(2-AZIDOBUTYRATE) – A NEW ENERGETIC AZIDO PLASTICIZER

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ABSTRACT

Dipropylene glycol bis(2-azidobutyrate) (DPG-BAB), a new energetic plasticizer has been synthesized via azidation reaction of the bromo precursor. The structure of the resulting compound, DPG-BAB, was confirmed by NMR-, RAMAN and IR-spectroscopic techniques.

The compound was also evaluated via thermal analysis. Mixtures of DPG-BAB and glycidyl azide polymer (GAP) were analyzed and compared with 2-[Butyl(nitro)amino]ethylnitrate (Bu-NENA) using also thermal analysis. Our preliminary evaluation of DPG-BAB shows that in mixtures with GAP this plasticizer, concerning glass transition temperatures, has a performance as good as Bu-NENA. However, DPG-BAB is not very energetic. Most benefit from this new plasticizer can be expected in gun propellant formulations where an insensitive, moderate energetic plasticizer with low glass transition temperature is needed. In such formulations DPG-BAB will lead to a specific energy which is in the same range like the gun propellant JA2 but with a combustion temperature that is around 700 °C lower.

Keywords: Dipropylene glycol bis(2-azidobutyrate); DPG-BAB; energetic plasticizer; azido plasticizer

INDRODUCTION

Energetic plasticizers (EP) are liquid organic compounds that are used to improve – like their non-energetic counterparts – the processability and mechanical properties of composite explosives and solid propellants [1]. In addition, EPs are intended to increase the energy output and influence the combustion behavior of such energetic materials [2]. To reach this goal EPs have various energetic groups (such as nitrate ester, nitro, nitramino, triazole, tetrazole, azido, etc.) in the molecules that enhance the specific impulse of propellants and the performance of explosives [3]. The increase in performance through the energetic groups is made possible by two action principles. Oxygen containing groups provide oxygen during the decomposition to drive the combustion or detonation process whereas nitrogen-rich azido groups release elemental nitrogen and considerable amounts of energy.

So far, nitrate ester-based EPs have been the most widespread, but they have limitations in terms of long-term stability and migration behavior [4]. Therefore, alternatives to nitrate ester-based EPs are being searched intensively. In this work we focused on a new azido-based EP because azido compounds are not expected to cause problems with stability and further the azido groups help to improve the energy content. The energy contribution per azido group in organic molecules depends on the type and structure of the molecule, but it is generally in the range of 356 kJ to 376 kJ per azide unit [5].

A common and useful method for synthesizing azido compounds is the halogen displacement reaction, where azide ions (N_3^- from sodium or lithium azide) displace halogen substituents (such as -Cl or -Br) or other leaving groups (such as tosylate or sulfonate) from organic precursors. This method has been chosen in the herein presented work for the synthesis of dipropylene glycol bis(2-azidobutyrate) (DPG-BAB) from its halogen precursor by nucleophilic substitution with sodium azide in DMSO leading to a novel EP.

RESULTS AND DISKUSSION

Table 1: Structural formula and some data of DPG-BAB

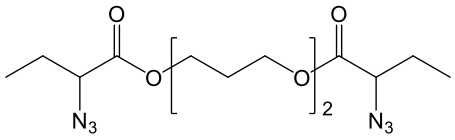
structural formula of DPG-BAB	chemical formula	$C_{14}H_{24}N_6O_5$
	molecular weight [g/mol]	356.38
	elemental analysis [%]	C, 47.18; H, 6.79; N, 23.58; O, 22.45
	oxygen balance (CO_2) [%]	-157.13

Table 1 shows the structural formula and some calculated data of DPG-BAB. This azido plasticizer belongs to the class of ether-ester compounds and with its polar ether and ester groups is expected that this EP will mix well with energetic binders such as GAP.

Spectroscopic data

Table 2: Spectroscopic data of DPG-BAB

spectroscopic method [unit]	results
IR [cm^{-1}]	2971 (m), 2938 (m), 2879 (m) (CH); 2102 (s) (-N_3); 1737 (s) (C=O); 1183 (s) (CO, ester); 1115 (m) (CO, ether)
Raman [cm^{-1}]	2939 (s); 2882 (s); 2809 (w); 2748 (w); 2109 (w); 1742 (w); 1445 (w); 1348 (w); 1291 (w); 1117 (w); 1089 (w); 1042 (w); 868 (w)
^{1}H NMR [ppm]	4.28 (td; COO-C**H$_2$**, 4H); 3.78 (dt; **H**C-N_3, 2H); 3.49 (m; **H$_2$**C-O-C**H$_2$**, 4H); 1.87 (m; H_3C-C**H$_2$**, CH_2-C**H$_2$**-CH_2, 8H); 1.02 (m; C**H$_3$**, 6H)
^{13}C NMR [ppm]	170.63 (**C**=O); 67.23, 63.52, 62.99 (H**C**-N_3, COO-**C**H_2, H_2**C**-O); 29.06, 25.00 (H_3C-**C**H_2, CH_2-**C**H_2-CH_2); 10.38 (**C**H_3)

The spectroscopic analysis (see Table 2) confirms the structure of DPG-BAB. All characteristic bands and peaks concerning the structure and the functional groups could be found and identified.

Thermal analysis with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

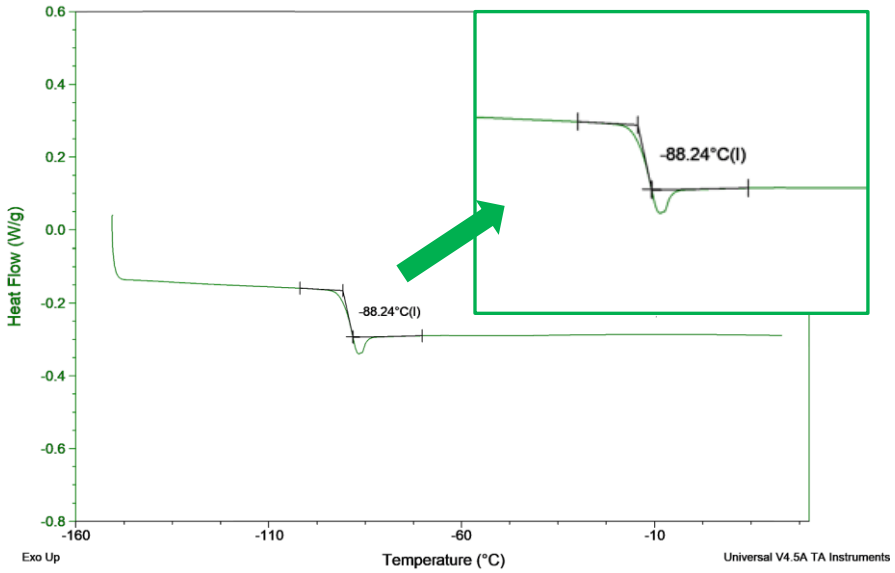


Figure 1: DSC glass transition measurement of DPG-BAB

The glass transition temperature of DPG-BAP is at a temperature of -88 °C, which is in a good range for a plasticizer.

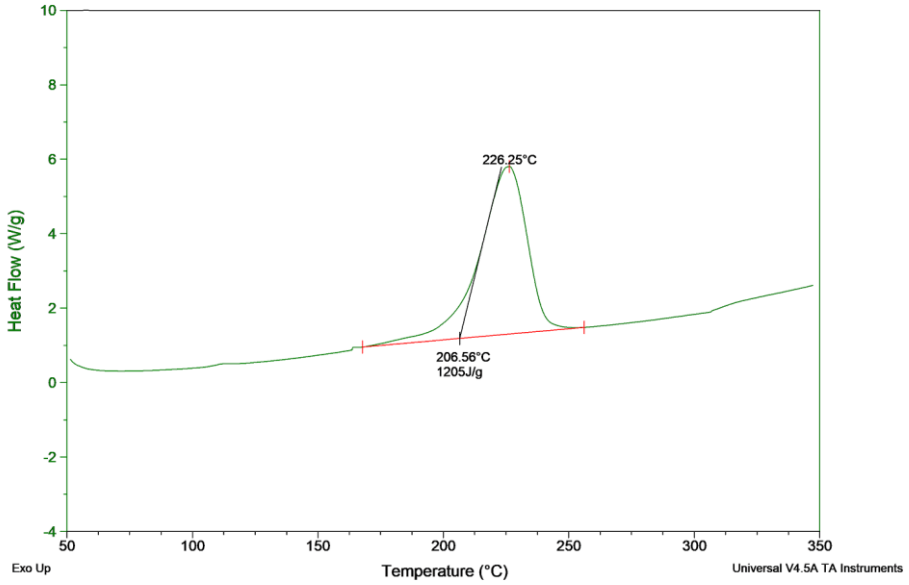


Figure 2: DSC measurement curve of DPG-BAB

The DSC measurement of DPG-BAB is shown in Figure 2. The measurement was performed in a high-pressure crucible F20. The DSC curve shows a single exothermic peak that starts at T_{dec} = 208.5 °C (onset value) with a peak maximum at 226.3 °C. This peak is caused by the decomposition of the azido groups which form elemental nitrogen N_2.

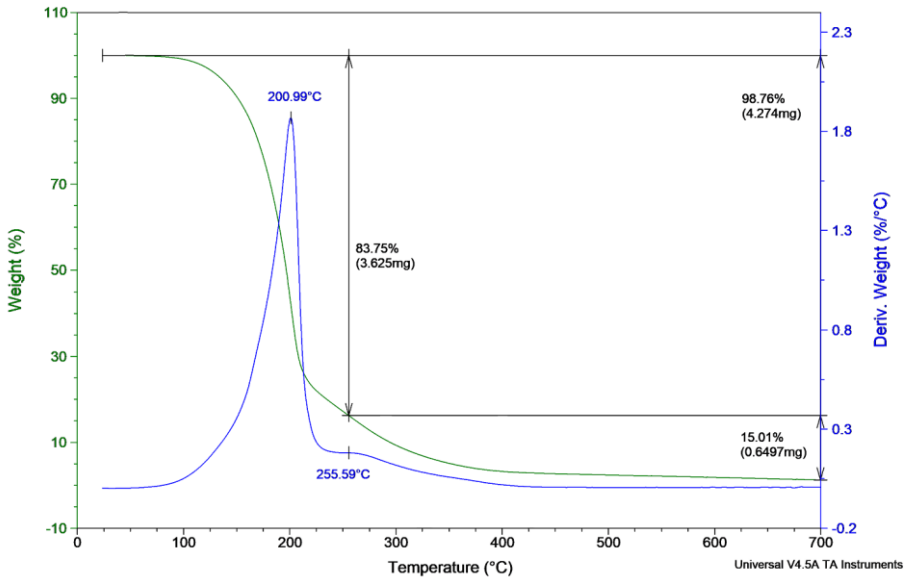


Figure 3: TGA measurement curve of DPG-BAB

The weight loss in TGA starts already at around 50 °C which does not coincide with the exothermic decomposition peak of the DSC. Such behavior indicates that this plasticizer may have a high vapor pressure or contain volatile by-products/residual solvents. The mayor weight loss step is then caused by the exothermic scission of the azido group forming molecular nitrogen which is typical for azido-compounds. The second step at around 256 °C is caused by the decomposition of the hydrocarbon chain of the molecule.

To check if the DPG-BAB shows reduced volatility when it is part of a formulation, we produced a mixture of GAP-Diol / DPG-BAB at ratio 60/40 (w/w) and performed TGA at isothermal condition (60 °C / 12 h).

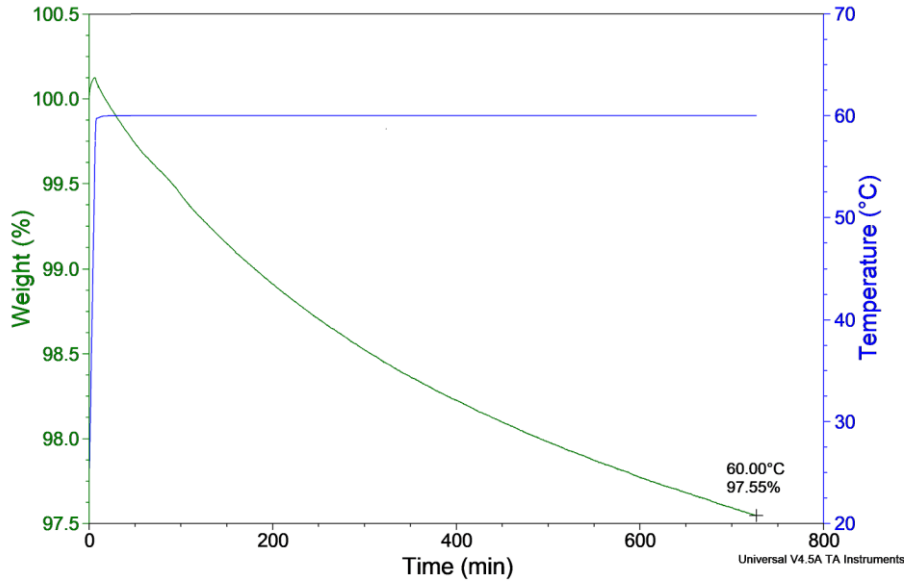


Figure 4: TGA of a mixture GAP / DPG-BAB at ratio 60/40 (w/w)

Surprisingly, the mass loss of the mixture is very low. In the TGA with its harsh measurement conditions of 12 h at 60 °C and a permanent stream of nitrogen passing over the sample, the weight loss was only 2.45 %. Apparently, DPG-BAB forms interactions with GAP that lower the vapor pressure of this plasticizer.

Finally, the plasticizing properties of DPG-BAB have been evaluated in mixtures with GAP-Diol and compared with Bu-NENA.

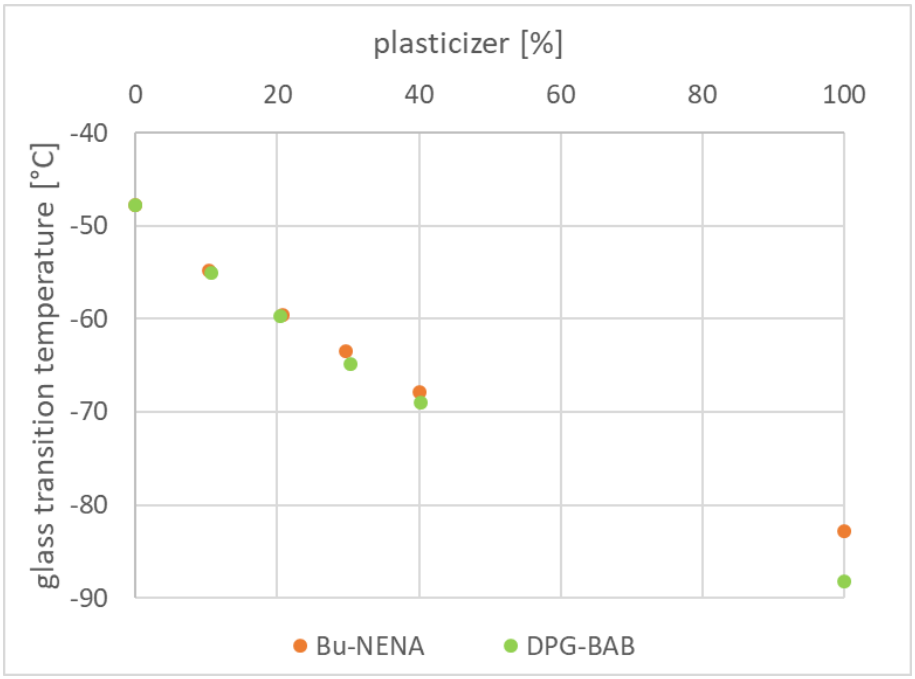


Figure 5: Glass transition temperatures (DSC) from mixtures DPG-BAB or Bu-NENA with GAP at ratios from 0/100 to 100/0 (w/w)

Figure 5 shows the glass transition temperatures (DSC) from mixtures DPG-BAB or Bu-NENA with GAP at ratios from 0/100 to 100/0 (w/w). Both plasticizers could lower the glass transition temperature of mixtures with GAP to a comparable amount. With plasticizer contents of 40 % (w) these GAP mixtures showed glass transition temperatures of -68 °C.

Comparison of DPG-BAB with modern EPs

DPG-BAB has been compared with several modern EPs. The following Figure 6 shows the structural formulas of these EPs.

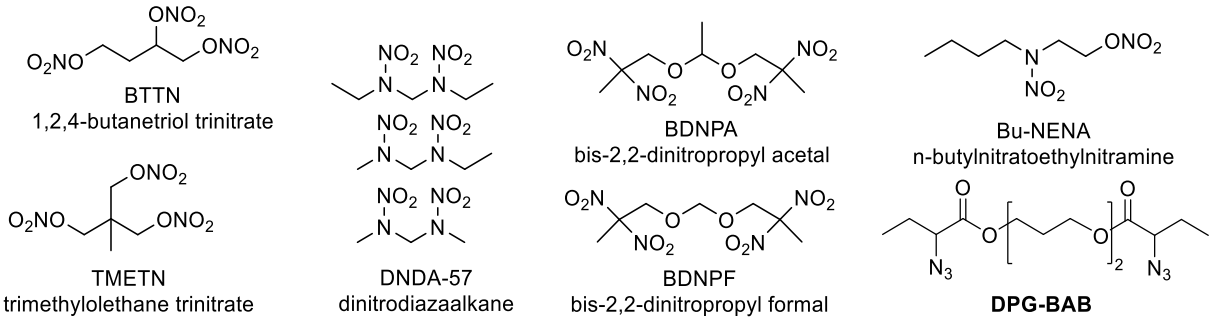


Figure 6: Structural formulas of modern EPs and DPG-BAB

Table 3: Comparison of conventional energetic plasticizers with DPG-BAB

	glass transition temperature (DSC) [°C]	decomposition temperature (TGA) [°C]	impact sensitivity [Nm]	heat of explosion[a] [J/g]	oxygen balance [%]	nitrogen content [%]	gas volume[b] [cm³/g]
BTTN	-65	156	1	6022	-16.6	17.4	634
TMETN	-62	155	1	5053	-34.5	16.5	794
DNDA57	-52	159	3	3848	-72.3	30.9	1078
BDNPA/F	-67	182	3	3469	-57.6	17.6	957
Bu-NENA	-82	152	6	3573	-104.3	20.3	1045
DPG-BAB	-88	201	>50	2042	-157.0	23.6	942

[a] calculated by ICT-Thermodynamic code (water liquid), [b] without H_2O at 25 °C

In Table 3 are listed some properties of several EPs in comparison to DPG-BAB. Of the plasticizers listed, DPG-BAB has the lowest glass transition temperature and is insensitive to impact loads. It also has the highest decomposition temperature. DPG-BAB has low values for heat of explosion and its oxygen balance. For further performance evaluation of DPB-BAB theoretical calculations with the ICT-Thermodynamic Code were conducted (DPB-BAB density 1.03 g/cm, heat of formation -357 kJ/mol).

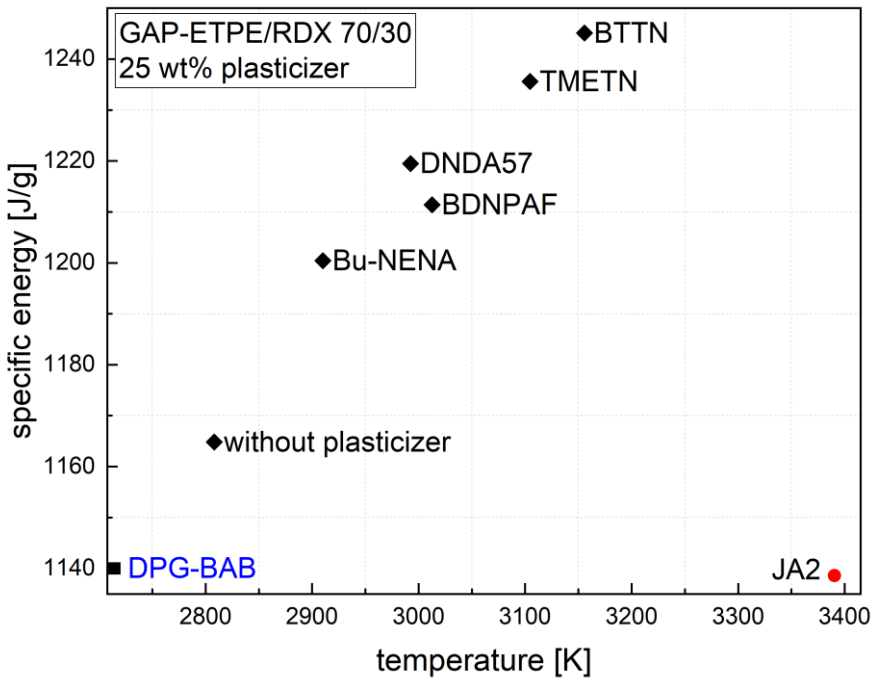


Figure 7: Performance evaluation of DPG-BAB and common EPs in an advanced gun propellant formulation in comparison to JA2

Figure 7 shows an overview of the calculated specific energies and the combustion temperatures of compositions of GAP ETPE/RDX (ratio 70/30 w/w) to which 25% (w) different plasticizers have been added. JA2 is also shown for comparison. The plasticizers with oxygen containing groups (nitrate ester, nitro, nitramino) lead to gun propellants with higher specific energies than this one from DPG-BAB. Even the basic composition (GAP-ETPE/RDX) without any plasticizer added has in the calculations a higher specific energy than the composition with DPG-BAB. However, the composition with this

plasticizer has the lowest combustion temperature which is beneficial in terms of gun barrel erosion. The specific energy of the formulation with DPG-BAB is in the same range as the gun propellant JA2 but with a combustion temperature that is nearly 700 °C lower.

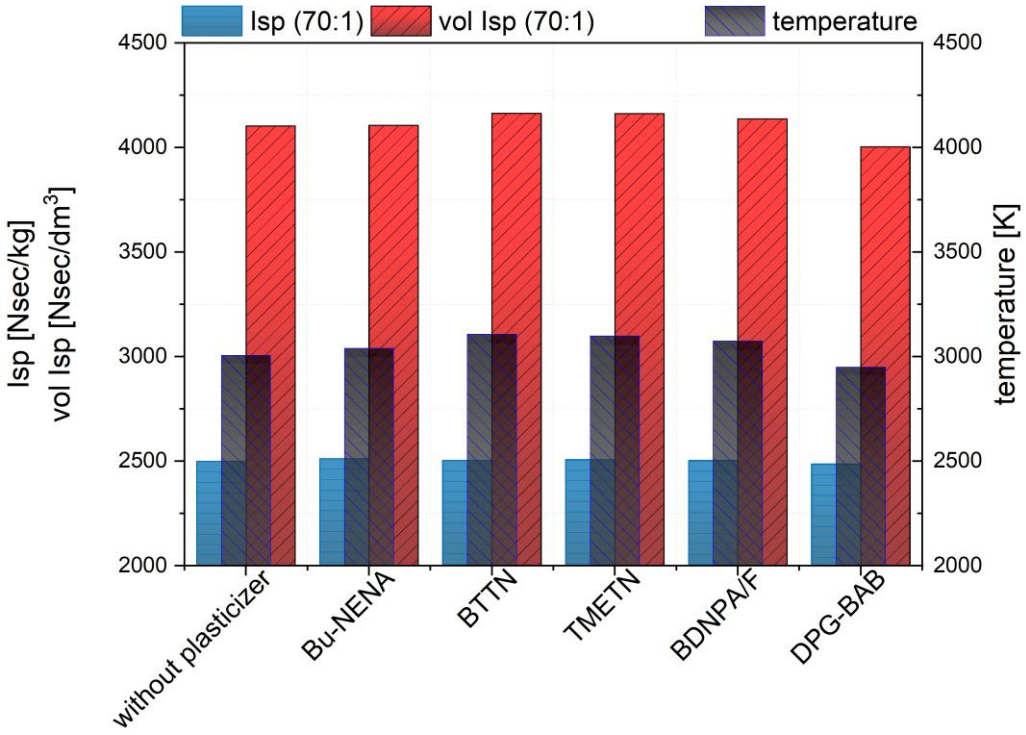


Figure 8: Performance evaluation of DPG-BAB and common EPs in an ADN-based rocket propellant composition

Figure 8 shows a comparison of the calculated Isp, the vol Isp and combustion temperatures of propellant formulations based on ammonium dinitramide (ADN) 75 % (w) and 25 % (w) GAP-binder. The GAP-binder contained 25 % (w) of different EPs. The calculation has been run with ICT-Thermodynamic Code using an expansion rate of 70:1 (frozen equilibrium). The results clearly show that DPG-BAB in the considered rocket formulations yields lower impulse performance than the compositions with the conventional EPs.

SUMMARY AND CONCLUSION

DPG-BAB as a new energetic plasticizer that belongs to the class of ether-ester compounds could be synthesized from its halogen precursor. The structure of DPG-BAB has been confirmed via spectroscopic analysis. The glass transition temperature of DPG-BAP is at a temperature of -88 °C, which is in a good range for a plasticizer. The DSC measurement of DPG-BAB shows a single exothermic peak that starts at T_{dec} = 208.5 °C (onset value) with a peak maximum at 226.3 °C. TGA measurements suggest that this plasticizer may have a high vapor pressure, however DPG-BAB shows reduced volatility when it is part of a formulation. The plasticizing performance of DPG-BAB on GAP is comparable to the plasticizer Bu-NENA.

Furthermore, the properties and calculated performance data of DPG-BAB has been compared with several modern EPs. Among the considered plasticizers DPG-BAB has the lowest glass transition temperature and the lowest sensitivity to impact loads. It also has

the highest decomposition temperature. However, DPG-BAB is not very energetic. This fact reflects on its performance data which has been calculated for a gun and a rocket propellant formulation. In both compositions DPG-BAB showed the lowest performance compared to the other EPs. Most benefit from this new plasticizer can be expected in gun propellant formulations where an insensitive, moderate energetic plasticizer with low glass transition temperature is needed. In such formulations DPG-BAB will lead to a specific energy which is in the same range as the gun propellant JA2 but with a combustion temperature that is around 700 °C lower.

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REFERENCES

[1] A. Provatas, Energetic Polymers and Plasticisers for Explosive Formulations: A Review of Recent Advances, Report DSTO-TR-0966 (2000), Defence Science and Technology Organisation, Melbourne Victoria, Australia
M. Ferrapontoff Lemos, M.A. Bohn, DMA of polyester-based polyurethane elastomers for composite rocket propellants containing different energetic plasticizers, J. Therm. Anal. Calorim. 2018, 131, 595–600

[2] M.A. Bohn, Determination of the kinetic data of the thermal decomposition of energetic plasticizers and binders by adiabatic self heating, Thermochimica Acta 1999, 337 121–139

[3] D. Kumari, K.D.B. Yamajala, H. Singh, R.R. Sanghavi, S.N. Asthana, K. Raju, S. Banerjee, Application of Azido Esters as Energetic Plasticizers for LOVA Propellant Formulations, Propellants Explos. Pyrotech. 2013, 38, 805–809
Y. Tang J.M. Shreeve, Nitroxy/Azido-Functionalized Triazoles as Potential Energetic Plasticizers, Chem. Eur. J. 2015, 21, 7285–7291
V.A. Hartdegen, Energetic Polymers and Plasticizers Based on Organic Azides, Nitro Groups and Tetrazoles, 2016, PhD Thesis at Department of Chemistry and Biochemistry, Ludwig-Maximilians-University of Munich
D. Drees, D. Löffel, A. Messmer, K. Schmid, Synthesis and Characterization of Azido Plasticizer, Propellants, Explos., Pyrotech. 1999, 24, 159–162
D. Kumari, R. Balakshe, S. Banerjee, H. Singh, Energetic plasticizers for gun & rocket propellants, Rev. J. Chem. 2012, 2, 240–262
J. Nešić, I.N. Cvijetić, J. Bogdanov, A. Marinković, Synthesis and Characterization of Azido Esters as Green Energetic Plasticizers, Propellants Explos. Pyrotech. 2021, 46, 1537–1546
U. Schaller, J. Lang, V. Gettwert, J. Hürttlen, V. Weiser, T. Keicher, 4-Amino-1-Butyl-1,2,4-Triazolium Dinitramide – Synthesis, Characterization and Combustion of a Low-Temperature Dinitramide-Based Energetic Ionic Liquid (EIL), Propellants Explos. Pyrotech. 2022, 47, e202200054

[4] X. Zou, W. Zhang, Z. Zhang, Y. Gu, X. Fu, Z. Ge, Y. Luo, Study on Properties of Energetic Plasticizer Modified Double-Base Propellant, Propellants Explos. Pyrotech. 2021, 46, 1–11

[5] M. Chiang, R. Wheeler, H-N_3 and CH_3-N_3 bond dissociation energies, Can. J. Chem. 1968, 46, 3785–3788

M. B. Frankel, L. R. Grant, J. E. Flanagan, Historical Development of Glycidyl Azide Polymer, Journal of Propulsion and Power 1992 8:3, 560–563
R. Xu, Z. Li, Y. Chen, J. Pei, J. Zhang, Enthalpy of Formation of p(BAMO)-b-GAP and Energetic Characteristics of Solid Propellants Based on the Copolymer, Propellants Explos. Pyrotech. 2021, 46, 969–974