

# DAP: A PROMISING NEW ENERGETIC CHAIN EXTENDER

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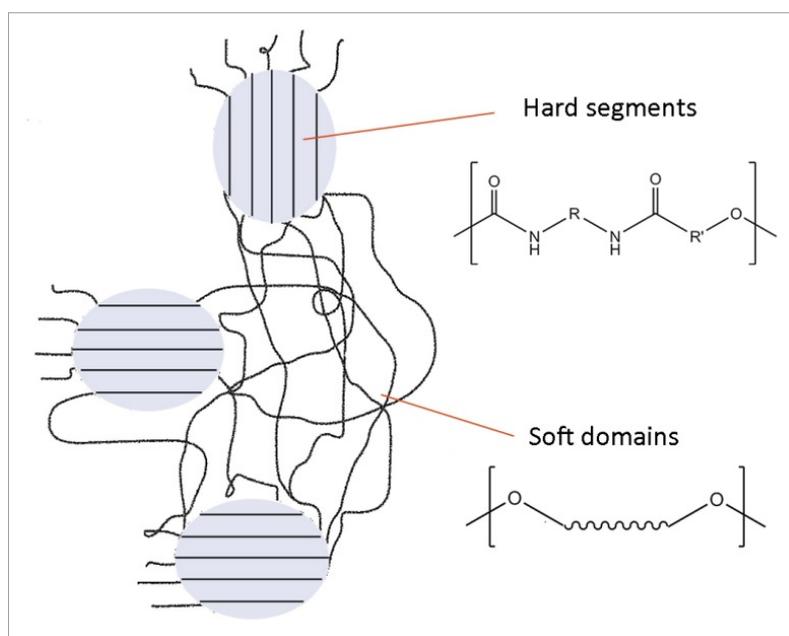
## ABSTRACT

2,2-bis(azidomethyl)propane-1,3-diol (DAP), a new energetic chain extender for energetic thermoplastic elastomers (ETPE) and different polymers made thereof are presented. An optimized synthesis procedure yielded pure, crystalline product that was extensively characterized. It could be shown that DAP is a promising building block for the synthesis of ETPEs with tailored properties for specific applications. Different polymers from DAP, glycidyl azide polymer (GAP) and two different isocyanates were prepared and characterized and their properties compared. Depending on proportioning and choice of isocyanates, a broad variety in consistency from rubbery flakes to sticky paste can be achieved. One specific ETPE was chosen for scale-up synthesis and its ability as binder for pressed polymer bonded explosives (PBX) was investigated. Based on HMX and TEX, a PBX formulation was developed and two formulations with said energetic binder and another one with paraffin wax as inert binder for comparison were manufactured. Pressing of cylindrical compacts yielded explosive charges with > 97 % TMD. Comparing explosive properties, the PBX with ETPE binder shows comparable detonation velocity but significantly increased detonation pressure. Shock wave sensitivity determined by GAP-test showed equal sensitivity values for both PBX at 20.4 kbar GO / 17.2 kbar No-GO.

## INTRODUCTION

In almost all applications of energetic materials, from gun and rocket propellants to explosives and pyrotechnics, the reactive ingredients are not used in their pure form. The crystalline particles often do not provide the required adhesion to form stable, uniform charges, additionally friction and shear forces amongst between the particles can generate accidental hot spots and thus lead to serious safety problems. To overcome these problems, the concept of plastic-bonded explosives (PBX) was introduced. The idea is to encapsulate each crystal of reactive material in a layer of binder, so that the binder acts as adhesive while at the same time separates particles from each other. This way, accidental hot spot generation is considerably reduced. Using an elastomeric system, the binder can act as cushion for shock or impact compression as well as attenuate huge forces acting on charges in ammunition while being shot out of a gun. By adjusting the composition and choice of binder and plasticizer, explosive charges of arbitrary dimensions and desired mechanical strength can be formed, from rigid pressings to thick pastes.

To this day, a variety of binders based on HTPB, *Estane*<sup>®</sup>, *HyTemp*<sup>®</sup> or *Viton*<sup>®</sup> A were developed to be used in explosive formulations. All these polymers have in common that they consist of completely non-energetic materials that dilute explosive energy and lower the overall performance of an energetic formulation. This way, high levels of explosives loading are needed to fulfill given performance requirements. Since the 1950s, research and development of energetic binders derived from energetic polymers was intensified. Contrary to inert binders, they liberate energy upon decomposition and contribute to the performance of an energetic formulation. This way, lower fractions of explosive solid filler are needed to give the same performance, which lowers sensitivity and allows softer formulations. Starting from well-known nitrocellulose, polymers with nitrate groups were investigated. To this day, a variety of energetic polymers is available, based on hydrocarbon backbones with well-known energetic moieties such as nitro-groups, nitramines or azides. A series of polyether-based energetic polymers were developed and one type based on epichlorohydrin emerged over time. Incorporation of an azide group into the former led to poly-(glycidyl azide), commonly known as glycidyl azide polymer (GAP). Its functionalities at the end of the GAP chains can be adjusted by different initiators and additives in the polymerization, yielding one or more hydroxyl groups on each end which can further react with isocyanate curing agents in curing.<sup>[1],[2]</sup> This way, GAP is an outstanding candidate for the synthesis of energetic thermoplastic elastomers (ETPEs) in cast cured formulations but also for the processing of ETPE-based propellants, explosives or pyrotechnics.



**Figure 1:** Schematic representation of the two-phase system in thermoplastic elastomers<sup>[1]</sup>

Thermoplastic elastomers are a special class of polymers and consist of hard (crystalline) and soft (amorphous) segments. In the former, reversible interactions like hydrogen-bonding or dipole-dipole interactions lead to the formation of rigid domains and chain association.

The latter segments exhibit considerably less interaction among each other and are immiscible with hard domains, so that microphase separation occurs. While the hard segments show thermoplastic behavior, the soft domains provide a certain amount of elasticity to the overall system.<sup>[3]</sup> The soft domains in thermoplastic elastomers based on polyurethane usually consist of hydroxyl-terminated

polyethers. Cross-linking with isocyanates builds urethane groups that form rigid segments, interacting via hydrogen bonding and VAN-DER-WAAL's forces.

Short polyvalent alcohols, e.g. butanediol or pentaerythritol, are typically used as chain extenders. They increase the size of rigid domains and are capable of building a 3-dimensional lattice. The physical properties of the final ETPE depend on the chain length of prepolymers, the choice of appropriate isocyanate curing agents and chain extenders as well as the ratio of isocyanate to hydroxyl groups. Using energetic polyethers as soft block prepolymers, energetic thermoplastic elastomers (ETPEs) can be synthesized which are particularly suitable as binders in explosives.

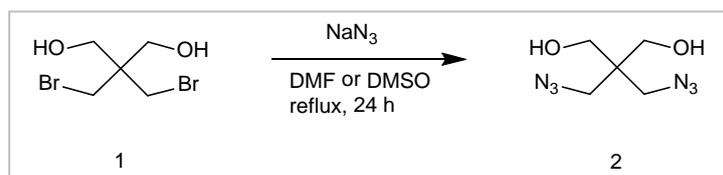
The synthesis of polyurethanes is typically catalyzed by organotin(IV) compounds, the most prominent being dibutyltin dilaurate (DBTL).<sup>[4]</sup> The reaction can be carried out in various solvents or in bulk. Since isocyanates are quite reactive towards water and other hydroxides, reactants as well as reaction atmosphere must be thoroughly freed from residual water and alcoholic solvents. The variety of energetic prepolymers, cross-linking agents and chain extenders offers building blocks with manifold possibilities to design ETPEs for different purposes.<sup>[5]</sup> DIAZ et al. investigated the mechanical and thermal properties of ETPEs based on GAP as a function of polyol chain extender and diisocyanate.<sup>[6]</sup> In their work, inert straight chain diols with four, five and six carbon atoms were used as chain extenders.

The motivation of this work was to optimize the synthesis of ETPE suitable as binder for high performance pressed explosive charges should be synthesized and fully characterized.

A new PBX formulation based on this ETPE was to be processed and characterized, and its processing should be optimized to yield high quality pressed charges. Ideally, the resulting explosive charges should exhibit sensitivity characteristics that allow their use in Insensitive Munitions (IM) applications.

## SYNTHESIS AND CHARACTERIZATION OF DAP

2,2-bis(azidomethyl)propane-1,3-diol (**2**), hereafter called **DAP**, is a promising candidate as energetic chain extender. Its structure with five carbon atoms and two symmetrically arranged azidomethyl moieties resembles the repeating unit of the energetic polymer poly-BAMO. A nitrogen content of 45.1 % ensures energetic properties, while two chemically equal primary hydroxy functions provide nucleophile sites that can react with polyisocyanates to built up macromolecular structures. Since the mid-1980s, a couple of publications described the molecule as it is a versatile building block not only in energetic materials research, but also in the area of medicinal, macromolecular and nanoscale chemistry.<sup>[7]</sup> The synthesis of DAP (scheme 1) is usually carried out by nucleophilic substitution of 2 bromine atoms in 2,2-bis(bromomethyl)propane-1,3-diol (**1**) with sodium azide in the polar, aprotic solvents DMF or DMSO. Reaction times of 24 hours and heating to reflux is required for maximum yield. A sophisticated work-up process is needed to obtain pure DAP without significant traces of the used solvent. In the mentioned literature, reported data on spectroscopic and physical properties differ widely.

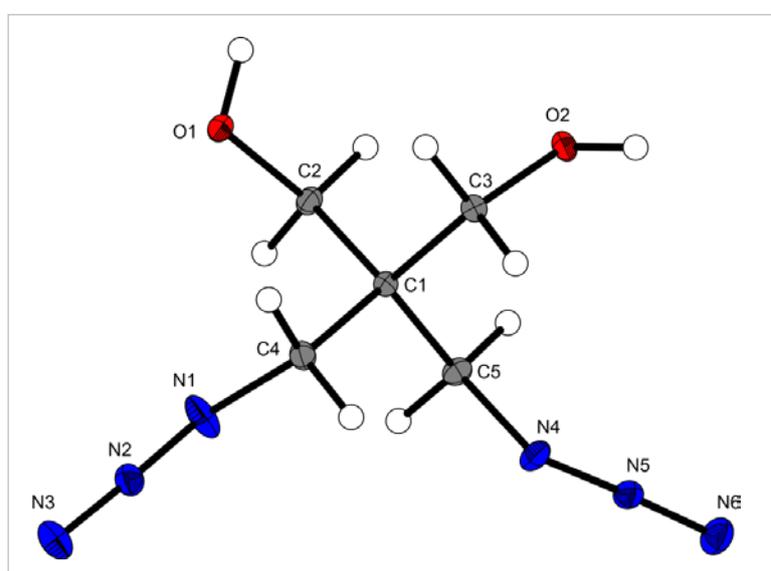


*Scheme 1: Standard Synthesis of DAP (2)*

To obtain **2** as pure as possible, the reaction was carried out in DMF and solvent was removed at elevated temperatures. Using a vacuum of  $10^{-6}$  mbar, DMF and desired product were separated by distillation. DAP was obtained as colorless crystals, which were characterized by NMR- and vibrational spectroscopy.

The sensitivity of DAP against shock and friction was examined BAM drophammer and friction apparatus according to NATO standard procedures.<sup>[8]</sup> Despite being a small molecule with two azide groups, DAP is quite safe to handle with a friction sensitivity of 324 N and an impact sensitivity of 25 J. The onset temperature of thermal decomposition was determined by DSC at 198.2 °C. The melting point of DAP was determined at 32.0 °C.

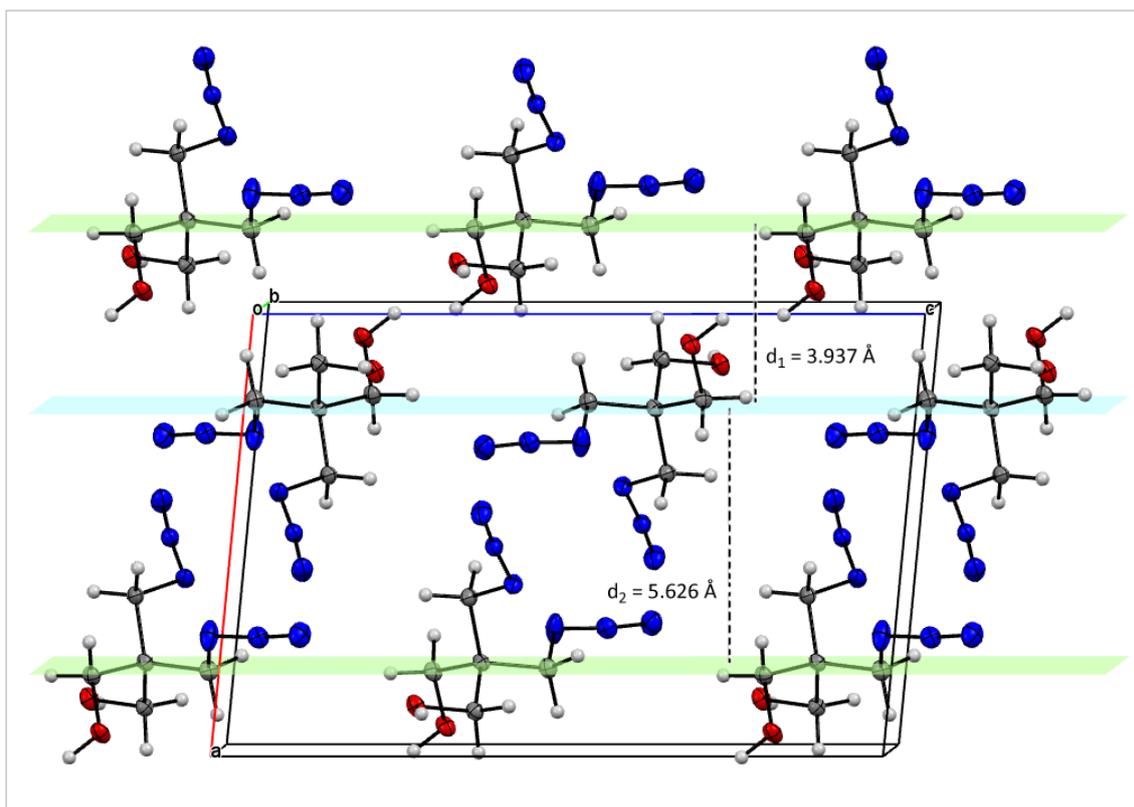
The crystals of DAP were additionally investigated by X-Ray single diffraction measurements. It crystallizes in form of colorless, clear, rod-shaped crystals in the monoclinic space group  $P2_1/c$  with a cell volume of 861.93 Å<sup>3</sup> and a density of 1.435 g/cm<sup>3</sup>. Figure 2 shows on asymmetric unit of DAP, four of which build the unit cell.



**Figure 2:** Molecular structure of DAP; thermal ellipsoids are set to 50 % probability. Symmetric operators: (i)  $x, y, z$ ; (ii)  $-x, 1/2+y, 1/2-z$ ; (iii)  $-x, -y, -z$ ; (iv)  $x, 1/2-y, 1/2+z$ .

All C-C and C-O bond lengths are well within the values expected. Bond angles found for the C-C bonds surrounding C1 are slightly distorted as two values are found: C2-C1-C5 and C3-C1-C4 show angles of 105.4° and 106.4°, whereas all other C<sub>x</sub>-C1-C<sub>y</sub> bond angles have values between 111.2°–111.6°. The azide moieties are slightly bent with an angle of 172.0° (N1-N2-N3) and 173.3° (N4-N5-N6) and show different torsion angles: The group of N1-N2-N3 is nearly in the plane defined by C1-C4-N1. In contrast, the other azide functionality N4-N5-N6 is twisted out of the C1-C5-N4-plane by 27°. The reason for these different torsions lies in the different environment of the nitrogen atoms: N5 has two neighboring nitrogen (N1 and N4) atoms from further units at a distance smaller than the combined VAN DER WAALS radii. Additionally, N6 interacts with two hydrogen atoms of further units and N4 with N5 of another molecule. In the group N1-N2-N3 only N1 interacts with N5 atoms of neighboring units.

The crystal structure of DAP can be described by alternating planes of asymmetric units built up by the central quaternary carbon atoms C1, where only one sort of functional groups is located on each side of the plane (fig. 3).



**Figure 3:** Expanded unit cell and formation of planes in the crystal structure of DAP; thermal ellipsoids are set to 50 % probability. Symmetric operators: (i)  $x, y, z$ ; (ii)  $-x, 1/2+y, 1/2-z$ ; (iii)  $-x, -y, -z$ ; (iv)  $x, 1/2-y, 1/2+z$ .

These planes are piled up so that sides with the same functional groups face each other. One of each azide groups (represented by N1-N2-N3) is arranged almost parallel to the described planes, whereas the other (N4-N5-N6) protrude in the space between both planes.

These nitrogen chains are oriented in a parallel way among each other, which explains the interactions between N4 and N5 as well as the different torsion angles described above. The distance between planes separated by bulky azide groups is 5.626 Å. They are connected by two short contacts N4-N5 with a distance of  $d(\text{N}\cdots\text{N}) = 3.096$  Å. In contrast, planes facing each other via hydroxyl groups are closer together with a distance of 3.937 Å. Strong intermolecular hydrogen bonding occurs amongst adjacent molecules via both hydroxyl groups where oxygen atoms O1 and O2 act as donor and acceptor. All donor-acceptor distances lie well within the sum of their VAN-DEER-WAALS-radii, and hydrogen bonds are nearly linear with angles of 179.7° and 173.7°.

Extensive work was put in finding a reliable and green alternative synthetic route to DAP. The main focus of this research was to explore an environmentally friendly solvent system, which ensures successful azidation, easy workup and at the same time lets the chemist get rid of problematic solvents DMF and DMSO. This work is currently in progress. Additionally, we could optimize the work-up process firstly described by Siebert et al. <sup>[9]</sup> This way, DAP crystals with a remaining DMF content of 0.3 mass-% could be obtained, with an overall yield of 72 %.

## SYNTHESIS OF ETPEs

To evaluate the suitability of DAP as energetic chain extender, a series of energetic thermoplastic elastomers was synthesized by DBTL-catalyzed solution polymerization with GAP-diol as energetic prepolymer. GAP-diol was purchased from SME France with  $M_w = 3946$  g/mol, polydispersity of 1.61 and an equivalent weight per mole OH-groups of 1180 g/mol.

TDI and paraphenylene diisocyanate (PDI) were chosen as diisocyanate curing agents because their molecular structure allows them to interact intermolecularly in the finished polymer via  $\pi$ -stacking interactions, building rigid hard segments. PDI is solid at room temperature and has a much lower vapor pressure than TDI, making it safer to handle. Dry THF was chosen as solvent since it does not react with any of the molecules used, and is easy to remove by evaporation. The composition and ratio of building blocks is shown in table 1; 10 g of each ETPE were synthesized.

*Table 1: Composition of DAP-based ETPEs (mass-%).*

	ETPE 4	ETPE 5	ETPE 6	ETPE 7
DAP	7.50	10.01	6.50	10.20
GAP	79.47	76.63	82.43	75.89
TDI	13.03	13.36	-	-
PDI	-	-	11.07	13.91

Progress of polymerization was monitored by IR spectroscopy of the reaction mixture. Decay of the asymmetric NCO stretching vibration at  $2270\text{ cm}^{-1}$  and growth of the carbonyl C=O stretching band at  $1729\text{ cm}^{-1}$  indicate the process of the reaction. Complete conversion of isocyanates to urethanes was observed after 48 hours. Figure 4 shows the resulting polymers. The resulting polymers offer a broad range of viscosities and elastic behavior. ETPE 4 is a paste whereas ETPE 5 is a firm, kneadable, clear rubber. Only ETPE 4 and ETPE 5 are totally clear, indicating a lack of large crystalline areas in the polymers. As expected, the polymers synthesized with PDI are turbid and more viscous compared to their TDI-analoga. ETPE 6 is a sticky paste with higher viscosity than ETPE 4. ETPE 7 was obtained as rubbery flakes that are not sticky. The different physical properties can be explained by the formation of more rigid hard-block domains in the elastomer: PDI molecules are symmetrical and rod-like structures that can form strong interactions among each other. This way, hard block segments with increased crystallinity are formed.<sup>[10]</sup> TDI in contrast is more bulky due to the meta-oriented second isocyanate-group and an additional methyl group. Analyzing the ETPEs by means of gel permeation chromatography, we can state that an increased content of DAP significantly reduces molecular weight and polydispersity, which leads to polymers with more rigidity/viscosity. Due to the different reactivity of isocyanate groups in TDI and PDI, the latter gave macromolecules with lower polydispersity and an overall higher molecular weight.



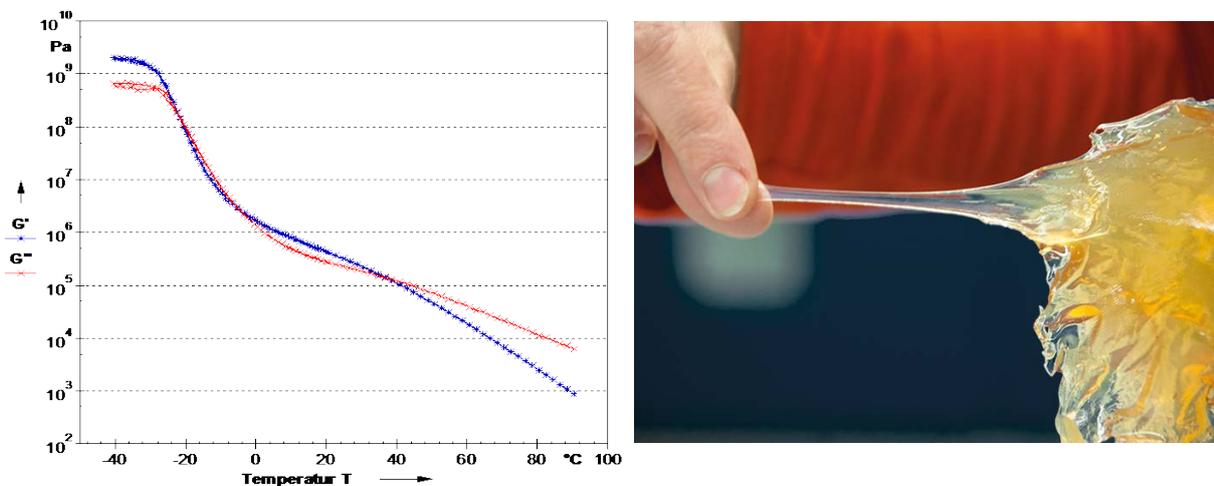
*Figure 4: Images of DAP-based ETPEs.*

No specific trend is observable in thermal behavior as glass transition points are in the close range of  $-34.9$  to  $-35.4$  °C. All DAP-based polymers are not sensitive towards friction as they do not show any reaction up to 360 N. Both PDI-cross linked ETPEs have a shock sensitivity of 15 J, whereas TPE 1 is slightly more (12.5 J) and ETPE 5 less (25 J) sensitive: Thermal decomposition of all polymers begins in a close range of 214 - 215 °C.

To prove the qualification of DAP-based ETPEs in energetic formulations, a high explosive formulation was to be designed, manufactured and processed. Of the ETPEs described above, ETPE 5 was chosen for scale-up and further processing. A batch of 100 g was synthesized and analyzed. Interestingly, the scaled-up polymer had almost twice the weight-average molecular mass and polydispersity compared to the small-scale synthesis. Accordingly, it forms a slightly more rigid rubber. These differences can be explained by an inadvertently incorporation of a slight excess of TDI, thus increasing the ratio of isocyanate to alcohol groups which leads to more cross-links in the final polymer.

The polymer was characterized in terms of dynamic mechanical analysis employing an oscillating rheometer with a frequency of 1 Hz over a temperature range from  $-40$  to  $+90$  °C. Storage and loss modulus are shown in figure 5. The moduli drop a factor of 1000 in the glass transition region between  $-30$  °C and  $-10$  °C and merge to a linear rubbery region up to 90 °C. The absence of rubbery flow and liquid flow regions is a sign of the semi crystallinity of the ETPE, and the slope indicates that only a moderate degree of cross-linking is present. No melting point can be seen. Heat of combustion of scaled-up ETPE 5 was determined by bomb calorimetric measurements to be -

20.68 kJ/g. Elemental analysis gives an empirical formula for 100 g ETPE 5 of  $C_{3.30}H_{4.69}N_{2.69}O_{1.19}$ .



**Figure 5:** left: Temperature dependent storage- (blue) and loss modulus (red) of ETPE 5. Right: Elastic, thread pulling behavior of ETPE 5.

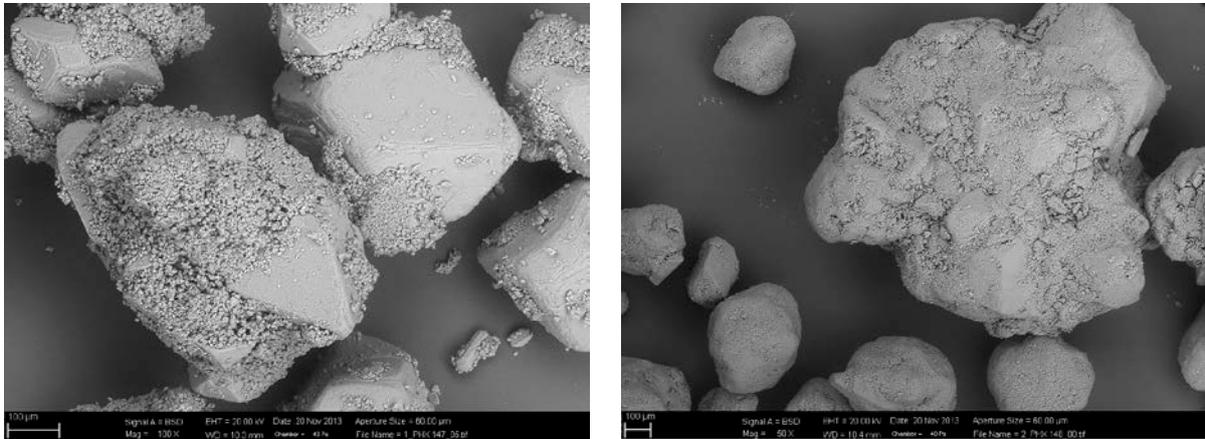
## PREPARATION AND PROCESSING OF PBX WITH DAP

The design of following PBX is inspired by the work of AUER et. al, who describe a molding powder based on a bimodal system of HMX particles that are mixed with a fine, insensitive explosive, e.g. TATB<sup>[11]</sup>. The authors describe that coating sensitive HMX with an insensitive additive leads to pressed charges with high explosive power and low sensitivity against shock waves. For this work, TEX (4,10-dinitro,2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane) was used as insensitive component besides HMX as main explosive. To obtain pressed charges with maximum density, particle size distribution was optimized by maximizing the tap density of mixtures with varying ratio of coarse and fine particles. TEX-content was selected to be in a range of between 4 and 5 mass-%. After optimizing the ratio of coarse and fine HMX reactions, fine tuning of the formulation with the appropriate amount of TEX was done to maximize density. 0.5 % graphite was added to the formulation to act as lubricant and reduce sensitivity against electrostatic discharge. Two PBXs were manufactured and tested, one with energetic binder (PBX 2) and one with paraffin wax with a melting range of 57 – 60 °C (PBX 1) as inert binder to compare explosive and sensitivity characteristics. ETPE 5 was chosen as energetic binder since its elasticity and physical properties seemed to make it the most suitable of all synthesized ETPEs for pressed charges. Binder content in each PBX was 4 %. Table 2 shows the overall formulation of the manufactured PBXs.

*Table 2: PBX formulation*

Component	Coarse HMX	Fine HMX	TEX	Graphite	Binder
Mean particle size	340 μm	18 μm	5 μm	-	-
Content [%]	68.6	22.1	4.8	0.5	4

Each PBX was manufactured using a horizontal kneader. The binders were dissolved in appropriate solvents and added to the solid contents. After intensive kneading and removal of the solvent, grey molding powders were obtained. SEM micrographs were made to examine coating and agglomeration of particles.



*Figure 6: SEM micrographs of PBX 1 (left) and PBX 2 (right).*

In the micrograph of PBX 1 (fig. 6), a substantial amount of free surfaces of HMX crystals is visible which shows that paraffin wax does not coat the surface of HMX properly. The adhesiveness is not satisfactory so that agglomeration hardly occurs and isolated small particles, probably TEX and paraffin wax, can be seen between coarse HMX particles. Crystals exhibit sharp corners and edges. In contrast, the micrograph of PBX 2 shows a number of large agglomerates with hardly any bare fine particles in between. All particles have rough surfaces and smooth, rounded corners and edges. The superior adhesiveness of ETPE 5 leads to completely coated particles that stick together in clusters up to 4 times larger than those in PBX 1. Smoothing of corners and edges results from binder coating, and to certain extent from the fact that the solvent used is capable of dissolving minimal amounts of HMX and thus rounds the particles, which favors processing.

With a value of 6 J, PBX 2 exhibits moderate sensitivity against shock whereas PBX 1 does not show reaction at impact energies below 15 J. Both are almost equally sensitive towards friction with 240 N (PBX 1) and 288 N (PBX 2). Stability at elevated temperatures and in vacuo were determined according to STANAG 4491. Auto ignition, measured with heating rate of 5 °C/min, occurred in both samples at a temperature of 254 °C. Dutch weight-loss tests as well as vacuum stability tests show that both PBXs are chemically stable and that no unwanted, dangerous reactions between the ingredients occur, making them safe for long-time storage. The theoretical maximum density of PBX 1 and 2 was calculated from the particle size ratios according to methods described by GERBER<sup>[12]</sup>. PBX 1 has a TMD of 1.803 g/cm<sup>3</sup> compared to 1.872 g/cm<sup>3</sup> of PBX 2 due to the higher density of ETPE 5. The plastic-bonded explosives described above were processed to cylindrical charges of 21 mm diameter using a two-sided, remote operated hydraulic press. For both molding powders, a press capacity of 87 kN (2.5 kbar) was chosen after preliminary tests. The compacts of both PBXs have a high density compared to their TMD with 99.2 % (PBX 1) and 97.4 % (PBX 2). The strength of the cylinders was compared by the amount of force needed to manually break them in half with a tool. PBX 1 cylinders are relatively brittle and break by application of moderate force whereas intense effort is needed to break PBX 2 charges, which have also a slightly higher Shore-hardness value.

## EVALUATION OF EXPLOSIVE PROPERTIES

To investigate explosive performance of pressed charges, combined VOD- and plate dent tests were conducted with two samples for each PBX. The charges were constructed of 19 compacts enclosed in cardboard tube, yielding an overall length of 40 cm. 12 coaxial sensors were placed in the central part of the charge, and ignition was ensured by a standardized 21 mm HWC booster. A massive ST37 steel witness plate was used to determine plate-dent test values. Sensitivity towards shock waves was determined by a modified small-scale test according to STANAG 4488. Detonation pressures were obtained from gap height with a calibration curve. Test results are summarized in table 3.

*Table 3: test results of explosive characterization*

	PBX 1	PBX 2
VOD [m/s]	8704.2 ± 8.2	8694.8 ± 10.5
Plate-dent [mm]	4.67 ± 0.03	5.25 ± 0.03
GAP-test GO	18 mm (20.4 kbar)	
GAP-test No-GO	19 mm (17.2 kbar)	

It can be seen that both formulations have almost equal VODs. The formulation with inert binder is slightly faster than the one with energetic binder, probably resulting from the lower density obtained in pressing. As indicated by the dent depth produced in the steel witness plate, PBX 2 develops a significantly higher brisance and detonation pressure, but in lieu of a calibration curve no absolute values in kbar can be given. Both formulations exhibit the same sensitivity towards shock waves. PBX 2 was expected to be less sensitive because of its elastic binder, which should cushion incoming shock waves to a certain extent. Increased binder content is probably needed for this effect to fully set in.

## SUMMARY

In search of new energetic chain extenders for energetic thermoplastic elastomers, 2,2-bis(azidomethyl)propane-1,3-diol (DAP) as promising candidate was synthesized in pure form for the first time. In contrast to descriptions in literature, it is not a liquid at room temperature but yields crystals that allowed single crystal X-ray measurements. Further characterization has been done by vibrational and NMR spectroscopy where literature data also was inconsistent. In search for an optimized synthetic process, an improved work-up process was developed, making it possible to obtain pure crystalline DAP without the need for special high-power vacuum equipment used before. Four different GAP-based ETPEs with DAP as chain extender were synthesized, and it could be shown that DAP is a promising chain extender. It allows tuning of mechanical properties of ETPEs depending on the desired application, from sticky pastes to rubbery flakes. One ETPE was chosen for scale-up and processing of pressed explosive charges. REM micrography showed that ETPE 5 has superior characteristics in coating and agglutinating solid particles in the molding powder. Pressing of cylindrical compacts yielded explosive charges with > 97 % TMD. Characterization of explosive properties shows that PBX with ETPE binder has comparable detonation velocity but significantly increased detonation pressure compared to PBX with inert binder. Additional work is currently in

progress to explore multiple binder systems with varying content of DAP and different diisocyanates for different applications. Additional optimization of binder content and pressing parameters is in progress to yield ETPE-bound pressed charges with higher density, VOD and to improve elasticity, resulting in significantly lowered shock-sensitivity.

## EXPERIMENTAL PART

All reagents were purchased from commercial sources and were, if not otherwise stated, used as is. HMX was purchased from *Dyno Nobel*. TEX was purchased from *Synthesisia*. GAP-Diol was purchased from *SNPE*. Infrared spectra were measured on a Thermo Scientific *Nicolet 6700 FT-IR* using a *Durascope Diamond ATR* unit. Raman spectra were obtained with a Bruker *RFS 100/S* with germanium detector. A *DSC Q1000* by TA instruments was used for DSC measurements. TGA was done on a *TGA Q 5000* by TA Instruments. Elementary analysis was performed on an *Elementar varioEL cube*. Melting points were determined on a Büchi *Melting Point B-540*. Particle Size analysis was done on a Malvern *Mastersizer 2000*.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were obtained on a Bruker *Advance 400* spectrometer at ambient temperature calibrated on residual solvent signals. The spectra were recorded at 400 MHz for  $^1\text{H}$  respectively 100 MHz for  $^{13}\text{C}$  resonance. Single crystal X-ray diffraction data were collected using an Oxford *Xcalibur3* diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a *Kappa CCD* detector. Data collection was undertaken using the *Crysalis CCD* software while structure solving was performed with *SHELXS-97* and refined with *SHELLXL-97*. Rheology data were determined with an Anton Paar *MCR 501* rheometer. Calorimetric measurements were performed with an IKA *C 2000* combustion calorimeter. A Zeiss *Supra 55 VP* was used to obtain SEM micrographs. Gel permeation chromatography was performed on a Agilent *Series 1100* with diode array detector. THF was used as eluent on PSS *SDV* Columns and polystyrene standards. Densities were measured on a Quantachrome *Ultrapycnometer 1000T*.

Shock sensitivity was measured on a BAM Fallhammer according to NATO STANAG 4489<sup>[8a]</sup>, friction sensitivity was determined via a BAM friction apparatus according to NATO STANAG 4487<sup>[8b]</sup>. Vacuum thermal stability (VTS), automatic explosion temperature (AET) and dutch weight loss test were performed according to NATO STANAG 4491<sup>[13]</sup>. Sensitivity against shock waves was measured with a modified GAP-test according to NATO STANAG 4488.<sup>[14]</sup> Detonation velocity was measured with an array of 12 coaxial sensors and recorded by an oscilloscope. Tap densities were characterized via an Engelsmann *STAV II volumeter*. Explosive formulations were mixed and kneaded in a remote-operated IKA *Duplex HKD 2,5* horizontal kneader. Pressing was performed with a remote-operated Hydrap *HS 125* two-sided hydraulic press.

## Synthesis of 2,2-bis(azidomethyl)propane-1,3-diol

2,2-bis(bromomethyl)propane-1,3-diol (50.00 g, 191 mmol) were dissolved in 200 ml DMF. Under continuous stirring, sodium azide (49.61 g, 763 mmol) were added gradually. The reaction mixture was heated to 120 °C and refluxed for 24 h. After cooling to room temperature, the formed precipitate was filtered off and washed with 30 ml DMF. 100 ml ethyl acetate were added to the filtrate and water was added until phase separation occurred. The mixture was extracted with ethyl acetate (5 x 100 ml) and the combined organic phases were washed once with 20 ml water. The organic phase was dried over MgSO<sub>4</sub> and evaporated. Solvent residues were removed by drying over 24 h with an oil vacuum pump at elevated temperatures. After standing at room temperature for one day, the resulting oil solidified to yield **1** as off-white, oily crystals (25.53 g, 130.3 mmol, 72 %).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) = 3.62 (d, J = 4.3 Hz, 4 H), 3.42 (s, 4H), 2.82 (s, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) = 63.4, 51.6, 44.8. IR: ν (cm<sup>-1</sup>) (rel. int.) = 3219 (m), 2943 (w), 2925 (w), 2101 (vs), 1461 (w), 1441 (m), 1382 (w), 1361 (m), 1273 (m), 1219 (w), 1145 (w), 1047 (m), 1030 (s), 1007 (m), 944 (m), 889 (m), 667 (m). **Elementary analysis** (C<sub>5</sub>H<sub>10</sub>N<sub>6</sub>O<sub>2</sub>): calc: C, 32.26; H, 5.41; N, 45.14; O, 17.19. Found: C, 31.98; H, 5.46; N, 43.96. **Mass spectrometry:** m/z (DEI+): 187.2 [M+H]; 159.2 [M+H-2N]; 129.2 [M-4N]; 98.2 [M-4N-2OH]. **Melting point:** 32.0 °C. **Sensitivities:** Friction: 324 N, Impact: 25 J. DSC (onset, 5 °C min<sup>-1</sup>): T<sub>Dec</sub>: 198.2 °C.

## Scaled-up Synthesis of ETPE 5

GAP diol (74.993 g, 31.78 mmol) was diluted in 300 ml dry THF. A solution of **1** (10.064 mg, 54.06 mmol) in 50 ml THF was added. Toluenediisocyanate (14.944, 85.89 mmol) and 0.4 ml of DBTL were added. The reaction mixture was stirred under nitrogen atmosphere for 48 h, the solvent evaporated and the resulting gel dried in a vacuum oven for 2 days. **ETPE 5** was obtained as clear yellowish, highly viscous gel.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) = 7.78 (br. s.), 4.99 (br. s.), 4.06 (br. s.), 3.17 - 3.81 (m), 2.86 (s), 2.55 (s), 2.12 (br. s.), 1.73 - 1.81 (m), 1.64 (s), 1.18 (s). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) = 78.7, 69.6, 51.7, 41.0. IR: ν (cm<sup>-1</sup>) (rel. int.) = 3324 (w), 2922 (w), 2875 (w), 2091 (vs), 1732 (m), 1600 (w), 1532 (m), 1445 (w), 1277 (m), 1221 (m), 1113 (m), 1065 (m), 1000 (w), 936 (w), 900 (w), 818 (w), 764 (w), 668 (w). **DSC** (onset, 5 °C min<sup>-1</sup>): T<sub>Dec</sub>: 214.5 °C; T<sub>g</sub>: -31.5 °C. **Elementary analysis:** calc: C, 41.36; H, 4.78, N, 37.06. Found: C, 39.61; H, 4.73; N, 37.72. **Sensitivities:** Friction: >360 N, Impact: 17.5 J.

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