NEW ENERGETIC THERMOPLASTIC ELASTOMERS FOR PRESSED EXPLOSIVE CHARGES

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ABSTRACT

Four different energetic thermoplastic elastomers (ETPEs) from glycidyl azide polymer (GAP) and isocyanates with 2,2-bis(bromomethyl)propane-1,3-diol (DAP) as chain extender were synthesized. It was proven that DAP is a promising monomer in ETPE synthesis, offering the opportunity to get elastomers with tailored hard-block segments and thus specific mechanical properties. Two aromatic diisocyanates for polyaddition were explored and the properties of the different ETPEs compared. A broad variety of consistency, from sticky paste to rubbery flakes could be obtained. One specific ETPE was chosen and characterized by means of temperature-dependant viscosity. A PBX formulation based on HMX and TEX was developed, and two formulations, one with ETPE as energetic binder and another one with paraffin wax as inert binder were manufactured. 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. Gap-test determined equal shock wave sensitivity of both PBX at 20.4 kbar GO / 17.2 kbar No-GO.

INTRODUCTION

To improve safety, performance, processability and mechanical strength, plastic-bonded explosives (PBX) were developed. In these formulations explosive particles are incorporated in polymeric binder systems and optional plasticizer. The concept is to encapsulate each explosive crystal 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 by friction or shear forces between the particles can be prevented and the binder acts as cushion for shock and impact compression, especially when an elastomeric binder is used. Additionally, huge forces acting on an explosive charge in ammunition while being shot out of a gun can be attenuated by an elastomeric system. 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 rubbery-elastic explosive sheets. However, blending energetic materials with non-energetic binder systems leads to dilution of explosive energy, and high levels of explosive loading are needed to fulfill given performance requirements. In the 1950s, research and development of energetic binders derived from energetic polymers was intensified. Contrary to inert binders, they liberate energy upon decomposing and contribute to the performance of an energetic formulation. This way, lower fractions of explosive solid filler are needed to fulfill performance requirements, which lower sensitivity and allow softer formulations.

An obvious candidate in this area is nitrocellulose (NC), first discovered in the 19th century and to this day extensively used for small rocket engines and gun propellants. However, NC shows several undesirable mechanical properties that could not be improved properly and hence no acceptable NC-based binder system for explosives could be developed [1].

To obtain modern energetic polymers, functional groups such as nitro, nitrato, or azido moieties are introduced into the polymer backbone. A series of polyether-based energetic polymers were developed and one type based on epichlorohydrin emerged over time. Incorporation of an azide functionality into the former led to poly-(glycidyl azide), commonly described as glycidyl azide polymer (GAP). 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 [1, 2]. So GAP can be used in cast cured formulations but also for the processing of ETPE-based propellants and explosives. Thermoplastic elastomers are a class of polymers that contain hard (crystalline) and soft (amorphous) segments (fig. 1). Reversible interactions like hydrogen bonding or dipole-dipole interactions lead to chain association and formation of rigid domains that are responsible for thermoplastic behavior. In contrast, soft segments exhibit less interaction among each other and are immiscible with hard domains so that microphase separation occurs. The soft segment matrix provides certain elasticity to the overall system [3].

The soft domains in thermoplastic elastomers based on poly-urethane usually consist of

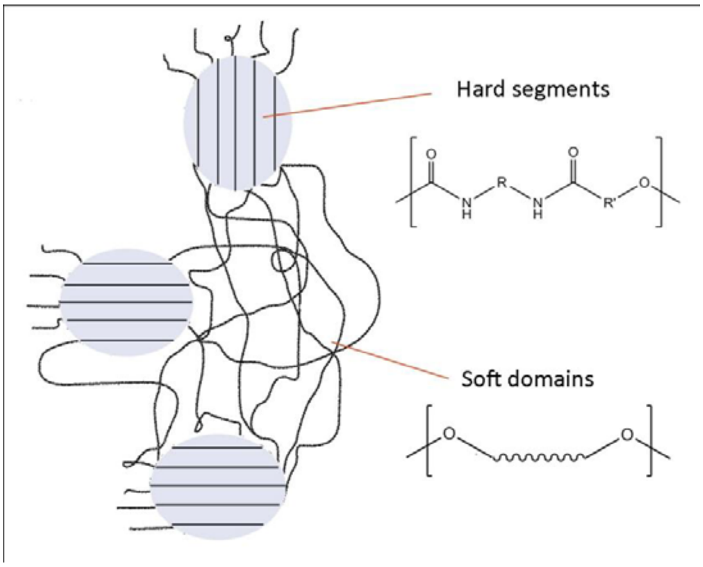


Figure 1: *Schematic representation of the two-phase elastomeric system in polyurethanes [1].*

hydroxyl-terminated polyethers. Cross-linking with isocyanates builts urethane groups that form rigid segments, interacting via hydrogen bonding and VAN-DER-WAAL's forces. Short polyvalent alcohols, e.g. BDO 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 an appropriate isocyanate curing agent and chain extender as well as the ratio of isocyanate to hydroxyl groups. Using energetic polyethers (like GAP) as soft block prepolymers, energetic thermoplastic elastomers (ETPEs) can be synthesized. As stated above, ETPEs are extraordinarily suitable as binders for explosives. Common diisocyanates used for curing ETPEs are shown in figure 2. Steric and electronic effects lead to substantial differences in reactivity between the isocyanate groups, not only comparing different molecules but also different sites in the same molecule. This fact is important to evaluate curing time and completion of the reaction.

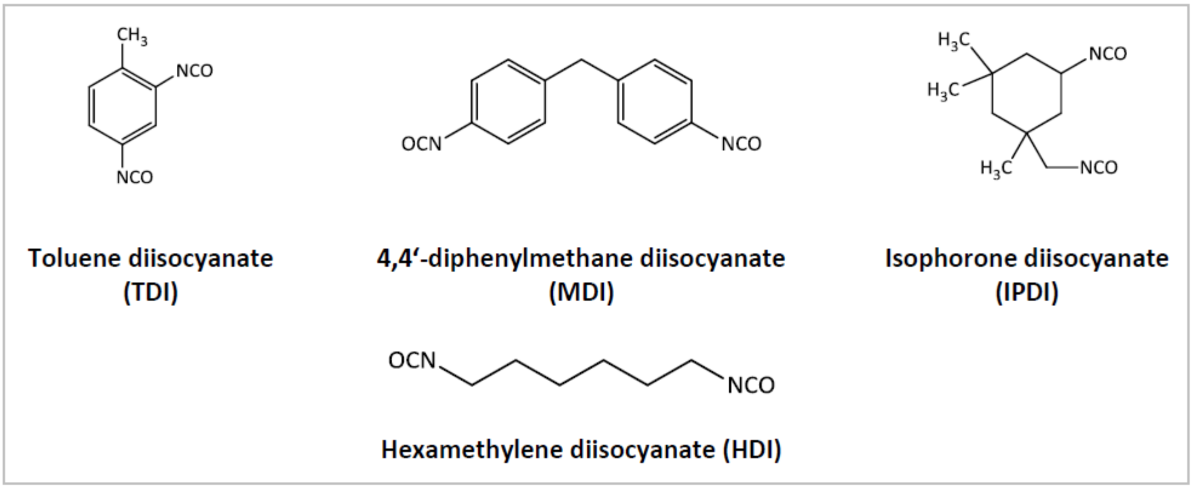


Figure 2: *Common diisocyanate curing agents.*

The synthesis of polyurethanes is typically catalyzed by organotin(IV) compounds, the most prominent being dibutyltin dilaurate (DBTL) [4]. 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.

To be used in energetic formulations, ETPEs should fulfill the following requirements:

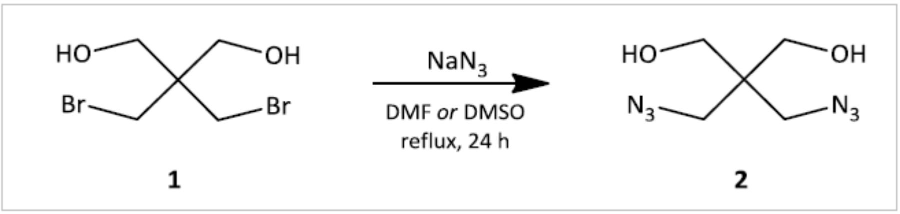
- Melting temperature in the range of 70 to 120 °C
- Low melt viscosity
- Glass transition temperature below -50 °C
- Physical and chemical compatibility with other ingredients of an explosive formulation and the casing
- High thermal stability
- Low sensitivity towards unintended stimuli
- Easy handling and processing

The variety of energetic prepolymers, cross-linking agents and chain extenders offers building blocks with manifold possibilities to design ETPEs for different purposes [3, 5]. Diaz et al. investigated the mechanical and thermal properties of ETPEs based on GAP as a function of polyol chain extender and diisocyanate [6]. 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 synthesize and fully characterize a GAP-based ETPE with DAP as chain extender, suitable as binder for high performance pressed explosive charges. 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 OF ETPEs

All energetic thermoplastic elastomers were obtained by solution polymerization of GAP-diol, with two different diisocyanates and with 2,2-bis(azidomethyl)propane-1,3-diol (DAP) as chain extender. Its structure with five carbon atoms and two symmetrically arranged azidomethyl moieties resembles the repeating unit of the energetic polymer poly-BAMO. The nitrogen content of 45.1 % ensures energetic properties while two chemically equal primary hydroxyl functions provide nucleophile sites that can react with polyisocyanates to build up macromolecular structures. DAP has been synthesized following a modified method described by Siebert et al. (scheme 1) [7].



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

GAP-diol was purchased from SME France with the following analytical data (obtained by GPC in THF):

Table 1: *Analytical data of GAP-diol*

Mw	3946 g/mol
Mn	2455 g/mol
PDI	1.61
Mp	2939 g/mol
Equivalent weight per mole OH-groups	1180 g/mol

Dry THF was chosen as solvent since it does not react with any of the molecules used, dissolves most of them readily and is easy to remove by evaporation. Dibutyl tin dilaurate (DBTL) was used as catalyst.

The composition and ratio of building blocks is shown in table 2. TDI and para-phenylene diisocyanate (PDI) were chosen as diisocyanate because their molecular structure allows them to interact intermolecularly in the finished polymer via π-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. Table 2 shows the composition of the synthesized ETPEs; 10 g were synthesized each. All components were thoroughly dried prior to use and the polymerization was catalyzed by DBTL.

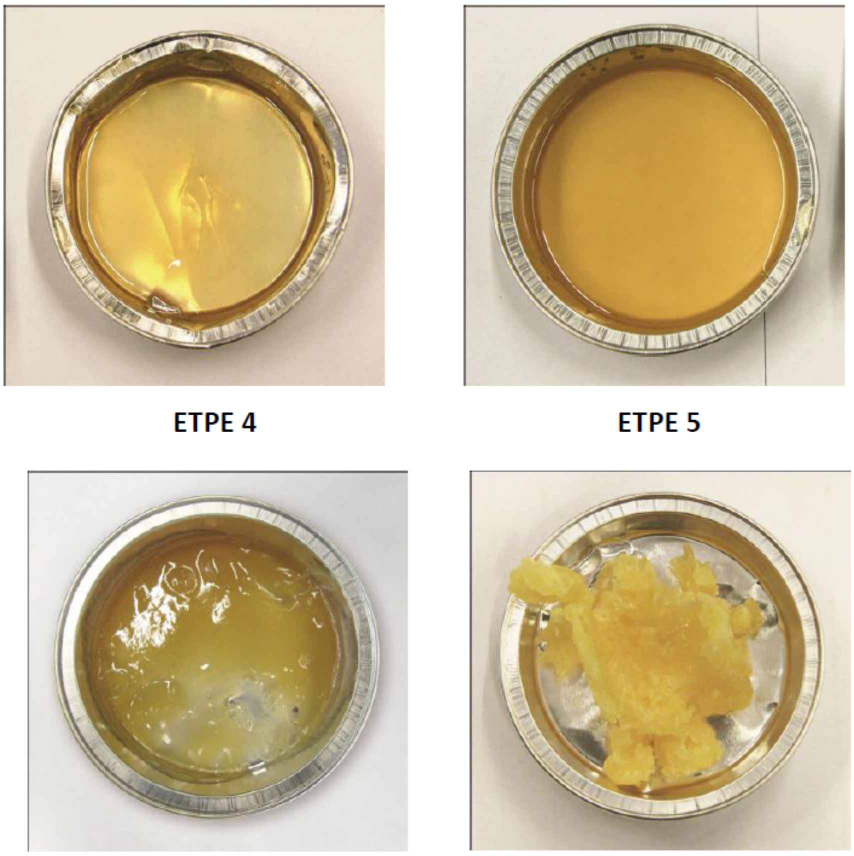
Table 2: *Composition of ETPEs (mass-%)*

	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

Since DAP, TDI and GAP are readily soluble in THF, no cosolvents were needed and the reaction mixture from ETPE 4 and 5 remained clear. In the synthesis of ETPE 6 and 7, PDI dissolved gradually and the reaction mixtures remained turbid over the complete reaction time. Progress of the polymerization was monitored by IR-spectroscopy of the reaction mixture. Decay of the asymmetric NCO stretching vibration at 2270 cm^{-1} and growth of the carbonyl C=O stretching band at 1279 cm^{-1} indicate the process of the reaction. The complete conversion of isocyanates to urethanes was observed after 48 hours.

Figure 3 shows the resulting polymers. 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 forms symmetrical, rod-like molecule that can form strong interactions among each other. TDI in contrast is more bulky since the second isocyanate-group is meta-oriented to the first, and the methyl group makes TDI more bulky. As described in literature, PDI forms hard block segments with increased crystallinity as compared to TDI [8].

No specific trend is observable in thermal behavior as glass transition points are in the close range of -34.9 to -35.4 °C and decomposition begins at 214 - 215 °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.



ETPE 4 **ETPE 5**

ETPE 6 **ETPE 7**

Figure 3: *Images of DAP-based ETPEs*

Based on previous unpublished investigations in our workgroup, ETPE 5 was chosen for scale-up and further processing. A second batch of 100 g was synthesized and analyzed. Interestingly, the scaled-up polymer has 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.

ETPE 5 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 4. The moduli drop a factor of 1000 in the glass transition region between -30 °C and -10 °C and merges to a linear rubbery region up to 90 °C. The absence of rubbery flow and liquid flow regions is a sign of the semi cristallinity of the ETPE, and the slope indicates that only a moderate degree of cross-linking is present. No melting point can be seen.

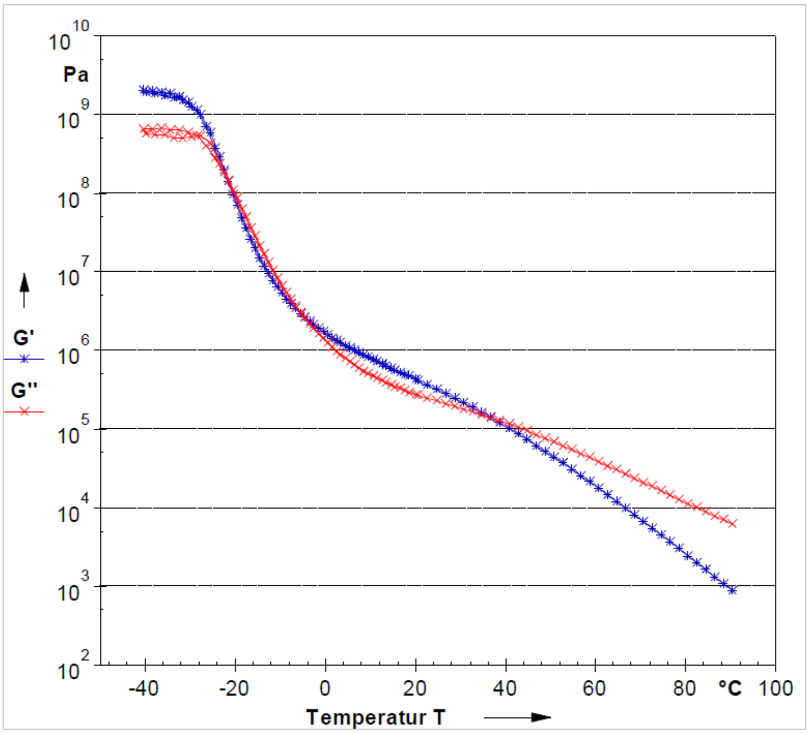


Figure 4: *Temperature dependant storage- (blue) and loss modulus (red) of ETPE 5*

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 $C_{3.30}H_{4.69}N_{2.69}O_{1.19}$.

MANUFACTURE AND PROCESSING OF PBX

To investigate the suitability of GAP- and DAP-based binder for pressed charges, a PBX formulation was designed and manufactured. The concept of the following PBX design is inspired by the work of AUER et al., who describe a bimodal system of coarse HMX particles that are mixed with a fine, insensitive explosive, e.g. TATB [9]. 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 was used as insensitive component besides HMX as main explosive. TEX or 4,10-dinitro,2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (fig. 5) is a highly strained heterocyclic nitramine which was first described by BOYER in 1990. It is easily accessible by two-step synthesis and offers high density and detonation velocity. Structurally related to CL-20, it offers less explosive power however is a lot less sensitive towards external stimuli [10].

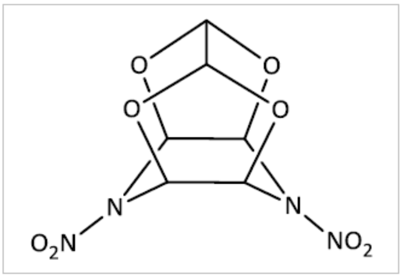


Figure 5: *Chemical structure of TEX*

Table 3 lists the particle sizes of materials used. 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-%. As starting point, a bimodal mixture of HMX particles was investigated and their maximum tap density was found at a mass ratio of 77.5 % coarse and 22.5 % fine particles. After addition of TEX, fine-tuning of particle ratio to maximize density led to the particle ratio described in table 3.

Table 3: *Particle sizes and ratio in PBX*

Material	**Mean particle size [µm]**	**Ratio in PBX [%]**
Coarse HMX	340.0	72
Fine HMX	17.5	23
TEX	4.8	5

0.5 % graphite was added to the formulation since it reduces sensitivity against electrostatic discharge and acts as lubricant while pressing. 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 4 shows the overall formulation of the manufactured PBXs.

Table 4: *Formulation of PBXs used.*

Component	**Content [%]**
Coarse HMX	68.6
Fine HMX	22.1
TEX	4.8
Graphite	0.5
Binder	4

Each PBX was manufactured by filling the solid contents into a horizontal kneader and adding a solution of binder in petroleum ether (PBX 1) or ethyl acetate (PBX 2). After intensive kneading and removal of the solvent, grey molding powders were obtained. REM micrographs were made to examine coating and agglomeration of particles. In the micrographs 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 micrographs of PBX 2 (fig. 7) show 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, but also from the fact that ethyl acetate is capable of dissolving minimal amounts of HMX and thus rounds the particles. From the viewpoint of processing, round particles are favorable in pressing because they flow better and less particles are cracked when pressure is applied.

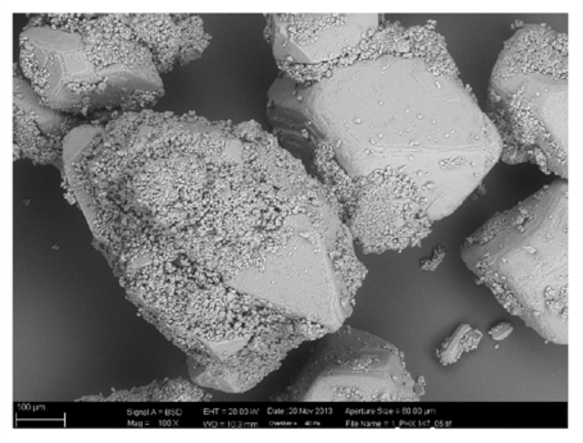


Figure 6: *REM Micrographs of PBX 1*

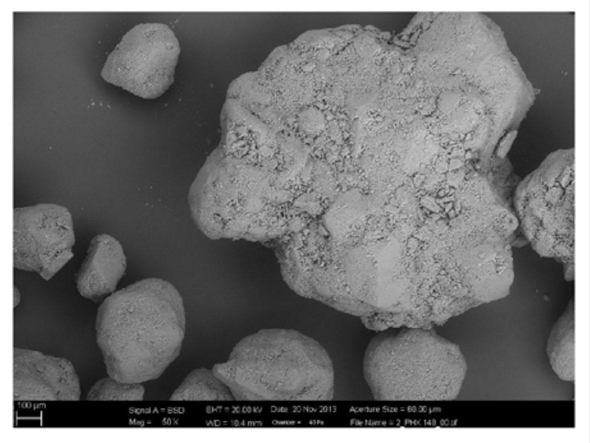


Figure 7: *REM Micrograph of PBX 2*

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 [11]. 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 [12]. PBX 1 has a TMD of 1.803 g/cm^3 compared to 1.872 g/cm^3 of PBX 2 due to the higher density of ETPE 5.

The plastic-bonded explosives described above were processed to cylindrical charges using a two-sided, remote operated hydraulic press. The cylinders were specified to be 21 mm in height and to have a diameter of 21 mm. Optimum press capacity was determined in preliminary tests where press capacity was increased until no substantial increase in density could be obtained. For both molding powders, a press capacity of 87 kN (2.5 kbar) was chosen.

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 a slightly higher Shore-hardness value.

CHARACTERIZATION 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; instead of water, PMMA disks were used as attenuator [13]. Detonation pressures were obtained from gap height with a calibration curve. Test results are summarized in table 10.

Table 10: *Test results of explosive characterizations.*

	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	19 mm (20.4 kbar)	
GAP-test No-GO	18 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.

EXPERIMENTAL PART

Apparatus and analysis

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 Synthesia. GAP-Diol was purchased from SNPE. Infrared spectra were measured on a Thermo Scientific Nicolet 6700 FT-IR using a Durascope Diamond ATR unit. 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. 1H and 13C-

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 1H respectively 100 MHz for 13C resonance. 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. Densities were measured on a Quantachrome Ultrapycnometer 1000T. Shock sensitivity was measured on a BAM Fallhammer according to NATO STANAG 4489 [14], friction sensitivity was determined via a BAM friction apparatus according to NATO STANAG 4487 [15]. Sensitivity against shock waves was measured with a modified GAP-test according to NATO STANAG 4488 [13]. Vacuum thermal stability (VTS), automatic explosion temperature (AET) and dutch weight loss test were performed according to NATO STANAG 4491 [11]. 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)

2,2-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 $MgSO_4$ 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 **2** as off-white, oily crystals (25.53 g, 130.3 mmol, 72 %).

^{1}H NMR (CDCl3): δ (ppm) = 3.62 (d, *J*=4.3 Hz, 4 H), 3.42 (s, 4H), 2.82 (s, 2H).

^{13}C NMR (CDCl3): δ (ppm) = 63.4, 51.6, 44.8.

IR: ν (cm^{-1}) (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 ($C_5H_{10}N_6O_2$): 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^{-1}): T_{Dec}: 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 DAP (10.064 g, 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.

^{1}H NMR (CDCl3): 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).

^{13}C NMR (CDCl3): δ (ppm) = 78.7, 69.6, 51.7, 41.0.

IR: ν (cm^{-1}) (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^{-1}): T_{Dec}: 214.5 °C; Tg: -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.

CONCLUSIONS

Four different ETPEs with DAP as chain extender were synthesized. It was proven that DAP is a promising monomer in ETPE synthesis, offering the opportunity to get elastomers with tailored hard-block segments and thus specific mechanical properties. Two aromatic diisocyanates for polyaddition were explored and the properties of the different ETPEs compared. It was shown that choice of diisocyanate as well as DAP-content influences the physical properties of the polymers. A broad variety of consistency, from sticky paste to rubbery flakes could be obtained. Further research is required to get polymers with glass transition points low enough to fulfill NATO STANAG requirements since the values obtained in ETPEs with DAP chain extender are around -35 °C.

One specific ETPE was chosen and characterized by means of temperature-dependant viscosity. A PBX formulation based on HMX was developed, and two formulations, one with ETPE as energetic binder and another one with paraffin wax as inert binder were manufactured. Investigation by means of 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. Further optimization of pressing parameters should yield ETPE-bound pressed charges with higher TMD and maximum VOD. Gap-test determined equal shock wave sensitivity of both PBX at 20.4 kbar GO / 17.2 kbar No-GO. Increasing the binder content in ETPE bound

PBX should increase the elasticity of explosive charges to cushion incoming shock waves, resulting in less shock-sensitive charges.

ABBREVIATIONS

ATR	attenuated total reflectance
BAM	Federal Institute for Materials Research and Testing - Berlin
BAMO	3,3-bis(azidomethyl)-oxetane
d	doublet
DSC	differential scanning calorimetry
ETPE	energetic thermoplastic elastomer
GAP	glycidyl azide polymer
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazinane
IR	infrared (spectroscopy)
J	coupling constant (NMR); Joule (sensitivity)
m	medium (IR); multiplett (NMR)
m/z	mass per charge (MS)
MS	mass spectrometry
N	Newton
PBX	plastic bonded explosive
ppm	parts per million (NMR)
q	quartet
RDX	1,3,5-trinitro-triazinane
s	strong (IR); singlet (NMR)
STANAG	Standardization agreement
t	triplet
TATB	triaminotrinitrobenzene
TEX	4,10-dinitro,2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane
Tg	glass transition temperature
TGA	thermogravimetric analysis
TMD	theoretical maximum density
w	weak (IR)

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