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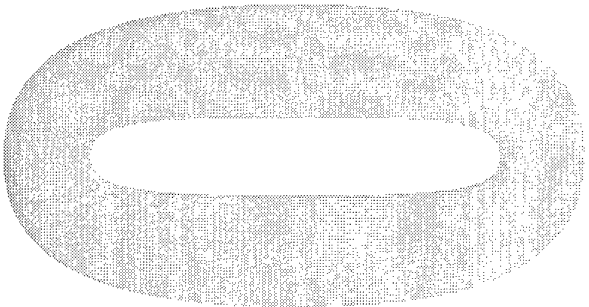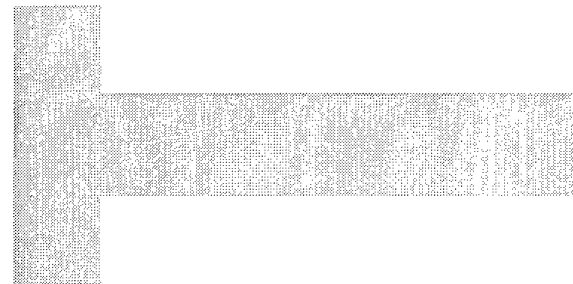
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Characterisation and Binder Studies of the Energetic Plasticiser - GLYN Oligomer

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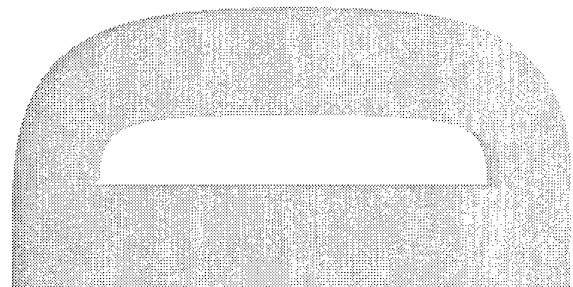
Characterisation and Binder Studies of the Energetic Plasticiser - GLYN Oligomer

Arthur Provatas

Weapons Systems Division
Systems Sciences Laboratory

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ABSTRACT

In an effort to comply with Insensitive Munitions (IM) criteria while minimising any reduction in performance, two part energetic binder systems which comprise an energetic polymer and an energetic plasticiser, are being developed for future use in PBX (polymer bonded explosive) fills in tactical missiles. Energetic binder systems confer energy output increases over conventional inert binder systems and are thus of interest to the ADF. Under a collaborative agreement with the UK, the ADF has received a new energetic plasticiser, GLYN oligomer, which promises to provide improvements such as higher energy output, good mechanical properties and low plasticiser exudation. This report serves to characterise the GLYN oligomer and examine its plasticising properties. Furthermore, comparison of migration data of the oligomer and other plasticiser(s) show that the GLYN oligomer is less likely to exude from PBX than other conventional plasticisers, thereby increasing the in-service life.

RELEASE LIMITATION

Approved for public release

AQ F03-11-2453

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Executive Summary

Current Polymer Bonded Explosives (PBX) formulated using inert, HTPB-based binder systems to meet Insensitive Munitions (IM) criteria suffer from low explosive performance in certain circumstances. Replacement of inert HTPB binders with energetic binder systems confers extra energy to the PBX while meeting IM compliant criteria. Furthermore, energetic binder systems also impart an increase in warhead performance (kill probability).

This report serves to characterise the energetic plasticiser, GLYN oligomer, which was provided under a UK collaborative arrangement with Dstl. Under this agreement Dstl was committed to provide WSD with research samples of a superior energetic plasticiser that has been developed specifically for use with the commercial energetic polymers polyGLYN and polyNIMMO, currently being studied by WSD.

This report describes the chemical, polymerisation and migration properties of the GLYN oligomer. Additionally, theoretical investigations of the plasticising properties will be examined.

Author

Arthur Provatas
Weapons Systems Division

Arthur Provatas graduated with a PhD (Chem. Tech.) from the University of South Australia in 1997 in polymer chemistry and commenced work for the Explosives Group, Weapons, System Division of DSTO investigating energetic polymers as binders, polymer bonded explosives and energetic thermoplastic elastomers for military applications. Dr Provatas is the Chemical Safety Officer for WSD and the Focus Officer for environmental issues with TTCP (The Technical Cooperation Program, KTA 4-28). Dr Provatas' multidisciplinary research has led him to publish research in polymer science, inorganic chemistry, chemical engineering, surface chemistry and orgainc synthesis.

Contents

Abbreviations

ADF	Australian Defence Force
AMRAAM	Advanced Medium Range Air-to-Air Missile
ASRAAM	Advanced Short Range Air-to-Air Missile
BDNPA/F	Bis(2,2-dinitropropyl)acetal/formal
BTTN	Butanetriol Trinitrate
BuNENA	Butyl-N-(2-nitroxyethyl)nitramine
D	Diffusion
DBTDL	Dibutyltin Dilaurate
Desmodur N100	Polyfunctional isocyanate
DSC	Differential Scanning Calorimetry
Dstl	Defence Science & Technology Laboratories
E_a	Activation Energy
ε	Plasticiser Efficiency
GAP	Glycidyl Azide Polymer
GLYN	Glycidyl Nitrate
GLYN oligomer	Oligomeric version of PolyGLYN
HMX	Cyclotetramethylenetetranitramine
HTPB	Hydroxyl Terminated Polybutadiene
IM	Insensitive Munitions
IPDI	Isophorone Diisocyanate
K10	Dinitroethylbenzene and Trinitroethylbenzene (65/35)
MEN42	Methyl Ethyl Nitrato Nitramine
NENA	Nitrato Ethyl nitramine
NMMO	2-Nitratomethyl-3-methyloxetane
PBX	Polymer Bonded Explosive
P_{CJ}	Chapman-Jouguet (Detonation) Pressure
PolyGLYN	Polymer of 2-nitratomethyloxirane
PolyNIMMO	Polymer of 3-nitratomethyl-3-methyloxetane
RDX	Cyclotrimethylenetrinitramine
T of I	Temperature of Ignition
Tg	Glass Transition Temperature
Tm	Melting Temperature
TMETN	Tetramethylopropane Ethane Trinitrate
VoD	Velocity of Detonation
XLD	Cross-link Density

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1. Introduction

DSTO has been involved with research into Polymer Bonded Explosives (PBX), in ordnance munitions for the ADF, over a number of years. Here at WSD, Explosives Group, we have considered the design of future PBX filled weapons systems incorporating energetic materials that have the preferred characteristics of low vulnerability, good mechanical properties, decreased signature, extended service life, and reduced environmental impact in the manufacture, disposal and use of PBX.

PBX technology utilises elastomeric binders, which are simply polymeric compositions, that act to bind together the various ingredients of a formulation. Binder systems typically consist of a polymeric binder with plasticiser(s), which act to improve processability and the mechanical properties of the PBX. The binder system imparts to formulations a lowering of vulnerability and for this reason are prime candidates for use in Insensitive Munitions (IM).

The Australian definition of IM reads "Insensitive Munitions (IM) are those munitions which reliably fulfil their performance, readiness and operational requirements on demand, but in which the violence of the response to unplanned hazardous stimuli is restricted to an acceptable level determined by (specified) test and response criteria" [1]. The Australian policy additionally states "IM are to be introduced into service with the Australian Defence Organisation, where it is sensible, practicable and cost-effective to do so".

In support of this policy, DSTO has initiated research that is covered in this report, into low vulnerability systems examining low sensitivity, PBX-based ordnance which contain energetic binders as a replacement for inert binders such as hydroxy-terminated polybutadiene (HTPB). The explosive formulations developed are intended for potential application in future generations of air-launched missile warheads such as ASRAAM.

In addition, the report is concerned with the nature of PBX plasticisers and in particular the detrimental ability of plasticisers to exude out of a PBX even under storage conditions. It is well known that if the plasticiser closely resembles the PBX polymeric binder, exudation can be lowered or reduced markedly. To test this hypothesis, a plasticiser with similar physico-chemical properties to its parent polymer was obtained and trialed for use in PBX systems. The plasticiser chosen was a Dstl/ICI research product called GLYN oligomer, which should offer material improvements to a PBX comprising polyGLYN as the polymeric binder.

Under a collaborative UK agreement, the ADF has received from the UK a new energetic plasticiser, the GLYN oligomer, which should enable improvements in energy output, good mechanical properties and low exudation with the binders. This report serves to chemically characterise the GLYN oligomer as well as examine its plasticising properties and cross-linking density. To test for exudation, kinetic investigations into the migration rate of the plasticiser in a polyGLYN binder matrix have been examined by isothermal thermogravimetric techniques and the results examined.

Understanding of this new, energetic plasticiser is paramount for continuing PBX work with energetic binder systems. GLYN oligomer should improve PBX properties particularly in reducing exudation while increasing energy output.

2. Background

A typical PBX contains between 75-85% energetics such as RDX or HMX with the remainder a binder, in a ratio of 50:50 polymer to plasticiser. Current in-service PBXs typically contain inert binder systems, that is the binder which contributes around 20% by weight of the final PBX composition, effectively diluting the potential energy output. Such inert binders include HTPB and polyacrylates. Next generation PBXs contain energetic binders, that is, the polymeric backbone contains explosophoric chemical groups such as nitro (C–NO$_2$), nitramine (N–NO$_2$), difluoroamino (-NF$_2$), azido groups (N$_3$), and nitrate esters (–ONO$_2$). These energetic binders impart an increase of energy output while lowering the vulnerability of the PBX. Figure 1 shows the chemical structures of several energetic polymers including: glycidyl azide polymer (GAP), poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO) and poly(glycidyl nitrate) (polyGLYN). Also shown is the inert binder HTPB. We have chosen polyGLYN as the parent polymer primarily because of its higher energy output over both GAP and polyNIMMO. The curing mechanism is via urethane formation by reaction of hydroxyl terminated polymers with an isocyanate cure agent.
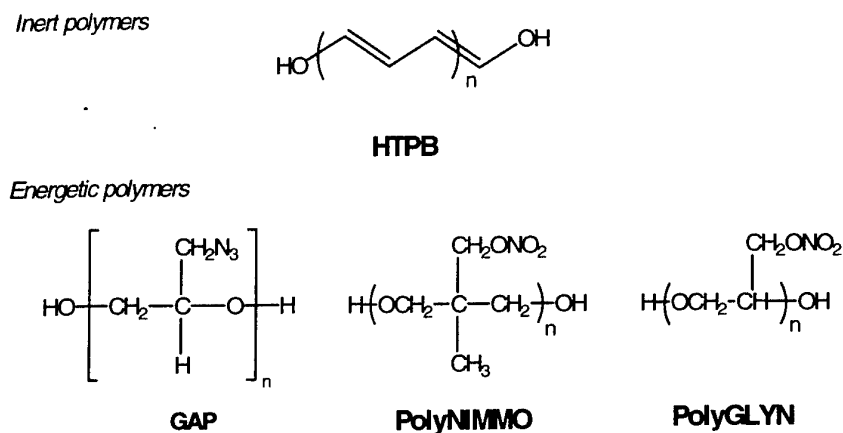

Figure 1: Energetic and Inert Polymers for use in Energetic Binder Systems

2.1 Energetic Plasticisers in PBXs

Plasticisers are used in energetic binder systems for PBXs to fulfil a number of requirements including:
- Lowering the viscosity to improve processing,

- Lowering the Tg (glass transition temperature) to improve mechanical properties,
- Altering the explosive performance of the PBX, and
- To improve safety of the PBX.

Most plasticisers that find use in PBXs commonly display exudation from the binder matrix even under storage conditions. This is highly undesirable since a degradation of mechanical and IM properties may result. It is well known that if the plasticiser closely resembles the PBX polymer, exudation can be lowered or reduced markedly. Use of polyGLYN in our PBX formulations has necessitated the use of GLYN oligomer, a plasticised version of the parent polymer. Furthermore, there is a inverse correlation between molecular weight and plasticiser mobility, the smaller the molecule the quicker it will exude through a polymer matrix. GLYN oligomer has a higher molecular weight than most energetic plasticisers including K10 and should reduce the migration of plasticiser through the polymer matrix. K10 is an energetic plasticiser comprising a 65/35 mixture of dinitroethylbenzene and trinitroethylbenzene.

2.2 Synthesis of GLYN Oligomer

GLYN oligomer is manufactured by ICI (Ardeer Site, Scotland) at pilot plant capacity via a three-step process [2]. The first step comprises the dinitrogen pentoxide (N_2O_5) nitration of glycidol to give the GLYN monomer followed by polymerisation with butanediol and catalyst (tetraflouroborate) (Figure 2). The polymerisation reaction is controlled by adjusting the catalyst/butanediol/GLYN monomer ratios. Such a polymerisation process will produce unwanted minor impurities as well as higher substituted oligomers. The oligomer is then subjected to N_2O_5 nitration again to convert free hydroxyl moieties to nitrato functional groups. Nitration gives improvements in oxygen balance and energy content and prevents unwanted reaction of the plasticiser with the isocyanate cross-linking agent.
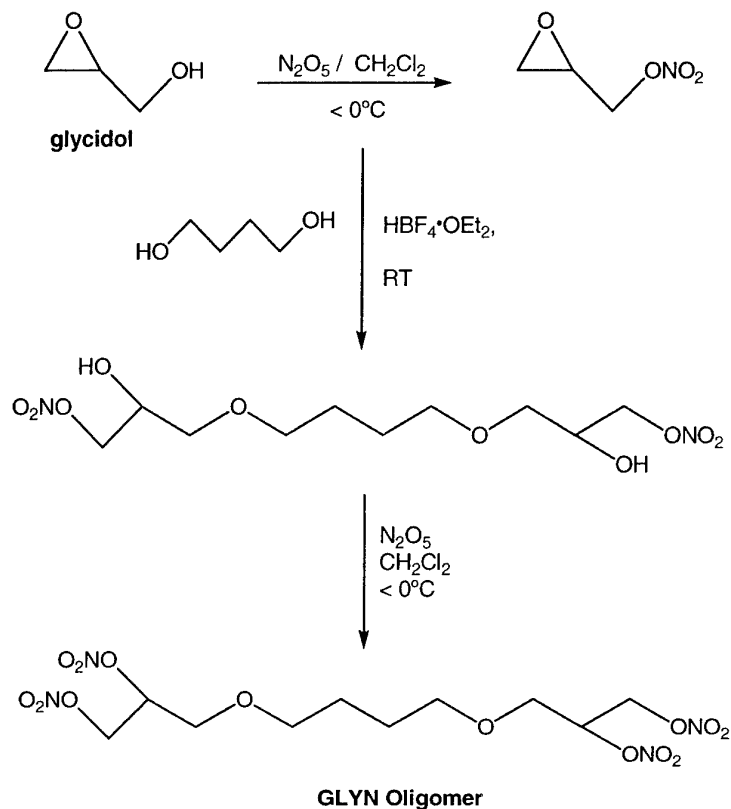
Figure 2: Synthetic Route to GLYN Oligomer

2.3 Diffusion Studies

A plasticiser's migration rate, or diffusion coefficient is of vital importance in establishing the service life of a PBX. A PBX that exudes a high amount of plasticiser is more likely to lead to problems with PBX safety and sensitivity. To determine the diffusion coefficient, isothermal thermogravimetric analysis (TGA) is employed. The use of this technique to determine the migration rates of energetic materials such as nitrocellulose propellants was first reported by Cartwright [3]. Cartwright [3] employed TGA to measure discs of a known geometry at elevated temperatures and which were held at a constant temperature for extended periods of time (typically 4000 mins). The method works by diffusion rates, whereby a loss in sample weight over an extended period equates to migration of plasticiser. A limitation of the technique is that it is generally accurate at obeying Fick's diffusion laws only during the early portion of TGA runs. Nevertheless, the technique is consistent with most types of plasticiser tested.

To compare Cartwright's investigations, values for the diffusion constant D, will be determined from weight loss, and rate decay constants over a temperature range for both K10 and GLYN oligomer plasticisers.

3. Experimental

3.1 Materials

PolyGLYN and GLYN oligomer were obtained from ICI Nobel Enterprises (Ardeer, Scotland) and degassed prior to use. The GLYN oligomer was shipped as a 5% solution of plasticiser in dichloromethane and solvent was stripped off under vacuum to leave a clear, yellow fluid of GLYN oligomer. K10 was purchased from Royal Ordnance, UK and used as received. Isocyanate curing agent isophorone diisocyanate (IPDI) was obtained from Bayer and distilled under reduced pressure to give a clear product. Desmodur N100, a polyfunctional isocyanate (functionality of 2.3), was also obtained from Bayer and used as received. Dibutyl tin dilaurate (DBDTL) is a cure-accelerating catalyst and was obtained from Aldrich and used as received.

3.2 Instrumentation

NMR analyses were conducted with a Varian Gemini Fourier Transform 200 MHz NMR spectrometer and associated software at the University of South Australia. All spectra were obtained in $CDCl_3$ or d_6-Acetone (Aldrich) as solvent and trichloromethylsilane (Aldrich) as internal standard. Number of transients for ^1H and ^{13}C NMR spectra were 16 and 2000 respectively. Infrared analyses (IR) were performed on a Perkin Elmer 683 infrared spectrometer on NaCl plates. Spectra were obtained over the wavenumber range 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1}.

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer Pyris 1 under nitrogen purge in closed aluminium pans. Glass transition temperatures (Tg) were carried out by cooling samples to –120°C for 1 minute and then heating to 20°C at 5°C per minute. The Tg was taken as the point of inflection of the specific heats for the glass and rubber phases of the binder and is an average of two measurements. Water was used as the reference for low temperature work. High temperature decomposition behaviour was measured by heating from 25 to 500°C at 5°C per minute with Indium metal as reference.

For diffusion studies, isothermal TGA analysis was carried out on a TA Instrument 2950 TGA at the Ian Wark Research Institute, University of South Australia. Weight ranges were calibrated over two points, one at ambient temperature and one at the Nickel Curie point (357.9°C). A heating rate of 10°C/min under a nitrogen atmosphere (50 mL/min) was used to obtain calibration points. Plasticised samples (containing 15% by weight plasticiser in a polyGLYN matrix) were contained in 70 μL alumina pans and degassed for several hours at 60°C and then allowed to cure for 7 days. Samples were then held isothermally at 83.0°C, 99.0°C, 115.0°C and 126.0°C for 4000 mins at each temperature under a nitrogen atmosphere (50 mL/min). Sample weights were normalized to initial weight = 100.

Mass spectral analysis was conducted at DSTO, Mariybyrnong on a Bruker BioApex II FT-ICR mass spectrometer. The sample was diluted 1000 times with methanol and directly infused into an electro-spray source at a rate of 300 µL per hour. The electro-spray source was operated in the positive ion mode. Eight scans were collected and summed, with a data set size 256K zero-filled to 512K. The instrument was externally calibrated with a mixture of trifluoroacetic acid and sodium hydroxide.

Absolute densities were determined using a Quantachrome Helium Ultrapycnometer 1000 by the procedure given in test 1 (absolute density determination) of [4]. Ultra high purity Helium gas (as supplied by BOC Gases) was used. The pycnometer was set for a maximum of 10 analyses. Volume of the sample is calculated via the following equation:

$$V_s = V_c - \frac{V_{exp}}{\frac{P_1}{P_2} - 1}$$

where V_s = sample volume
V_c = cell volume
V_{exp} = expansion volume
P_1 = initial pressure
P_2 = pressure after expansion

Density is automatically calculated by the pycnometer.

3.3 Preparation of Isocyanate Cured Rubbers

To examine the physico-chemical properties of the polyGLYN/GLYN oligomer and K10 binder systems, a series of rubbers were cured without the incorporation of energetics such as RDX or HMX (Table 1). The binder systems were cured with a 50:50 N100/IPDI mixture at a ratio of 1.1:1 isocyanate/polymer hydroxyl with the addition of 5ppm dibutyl tin dilaurate as catalyst. Binder formulations were prepared by degassing polymer and plasticiser in an oven at 60°C for 16 hours. The binder was then mixed in a glass beaker with isocyanate plus catalyst until homogeneous and degassed for 1 h at 60°C under vacuum. The binder was cast into Teflon moulds (11.0 cm × 6.0 cm × 1.5 cm) sealed at one end with putty and degassed at 60°C under vacuum until gas evolution ceases. The vacuum was released and binder left to cure at 60°C for 7 days. Fingers of cured binder were then removed (see Figure 3) and analysed for hardness, thermal properties, hazard properties and stability.

Table 1: *Unfilled PolyGYLN/GLYN Oligomer Binder Systems (at differing plasticiser % levels). All formulations contain 5ppm dibutyl tin dilaurate as catalyst.*

Binder System (Polymer/Plasticiser)	PolyGLYN	K10	GLYN Oligomer	N100/IPDI
PolyGLYN/K10				
AP0402-01	12.8	5.0 (25%)	–	1.35/0.85
AP0402-02	13.4	6.6 (33%)	–	1.2/0.76
AP0402-03	8.53	10.0 (50%)	–	0.9/0.6
AP0402-04	6.6	13.4 (67%)	–	0.6/0.4
PolyGLYN/GLYN oligomer				
AP0402-05	12.8	–	5.0 (25%)	1.35/0.85
AP0402-06	13.4	–	6.6 (33%)	1.2/0.76
AP0402-07	8.53	–	10.0 (50%)	0.9/0.6
AP0402-08	6.6	–	13.4 (67%)	0.6/0.4

Note that the 67% plasticised rubbers failed to cure adequately for both plasticised systems. These particular formulations were repeated again without any further success in curing.
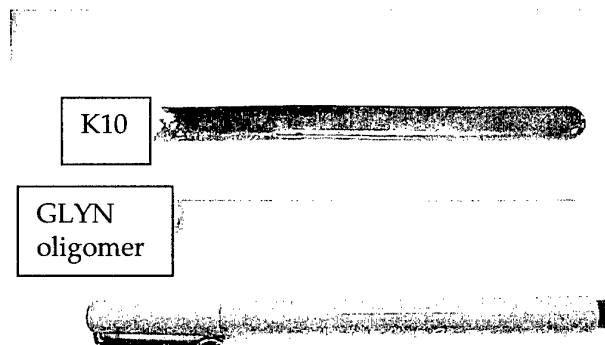

Figure 3: *PolyGLYN/K10 and PolyGLYN/GLYN Oligomer Fingers After Removal from Mould.*

3.4 Hazards and Mechanical Properties Testing

3.4.1 Temperature of Ignition

Temperature of ignition (T of I) was determined on an instrument built to specification [5]. Samples of 200 mg in glass test tubes were heated at 5°C/min till ignition or fast burn occurred, as defined by first visible signals such as smoke/flame or audible hiss/bang. The T of I is the temperature at which these events occur.

3.4.2 Vacuum Stability

Duplicate 2.0 g samples were placed in glass sample tubes, which were then attached to a mercury-filled manometer and evacuated [6]. The sample tubes were then placed in a heater bath at 100°C and a 1 h period was allowed for temperature equilibration. The volume of gas evolved was monitored for 40 h at 100°C and is measured as the average of duplicate samples.

3.4.3 Hardness

The ASTM-D2240 method was used to assess Shore "A" hardness [7]. A Shore A-2 Durometer with a Shore Conveloader test stand, which uses a hydraulic cylinder to control the rate of application of the indenter to the sample, was used with the standard 1 kg weight.
Hardness measurements were performed on the top surface at a distance of between 6 mm and 12 mm from the edge. Variations in hardness along a surface from centre to edge were found to be insignificant for respective surfaces. Five indentations per assessment were performed at ambient room temperature and each indentation was held for 30 s or until a constant hardness reading was obtained.

3.4.4 Cross-link Density Determination

The binder's soluble fraction (sol gel) and cross-link density (XLD) were determined by Soxhlet extraction of the binder with dichloromethane (see Appendix A for a full description of the method and equations used to determine sol gel and XLD).

4. Results and Discussion

The energetic plasticiser, GLYN oligomer, has been characterised for its physico-chemical properties by infrared spectroscopy, density, NMR spectroscopy, thermal analysis and mass spectral analysis. Additionally, hazard sensitivity properties have also been measured.

4.1 Physico-chemical Properties

4.1.1 IR Analysis

Infrared spectroscopy analysis shows the same functional groups as for the parent molecule, PolyGLYN (Table 2) [8]. The nitrato functionality for both oligomer and polymer is found at 1640 and 1280 cm^{-1}. Absorbances in the 3450 cm^{-1} range are evidence of O-H species while absorbances at 2890 and 1460 cm^{-1} are characteristic of organic backbone functionalities (C-H).

Table 2: IR Absorbances for GLYN Oligomer

Plasticiser	Wavenumber, v, cm^{-1}	Assignment	Intensity*
GLYN oligomer			
	2890	C–H	s
	1640	$O–NO_2$	s
	1460	C–H	m
	1390	NO_2	m
	1280	$O–NO_2$	s
	1100	C–O	s

* Intensity: s = strong; m = medium; w = weak.

4.1.2 Density

Relative density measurements have been recorded by a Helium Ultrapycnometer and results displayed in Table 3. Result closely matches expected literature value.

Table 3: Relative Density of GLYN Oligomer

Plasticiser	Measured Density, g/cm^3	Literature Density, g/cm^3
GLYN oligomer	1.39	1.38 [2]

4.1.3 NMR Spectroscopy

The GLYN oligomer plasticiser is synthesised via a cationic polymerisation process, with this type of reaction process tending to favour reaction with any impurities (if

present) [9]. NMR studies of the GLYN oligomer reveals the presence of impurities that may have arisen from impurities in the monomer (Figures 4 and 5). Impurities are likely to be a consequence of the starting material – glycidol. Hence the purity of the starting material must be ascertained prior to polymerisation and the glycidol must be freshly distilled and passed over molecular sieves. Impurities likely after polymerisation include mono-substituted butanediol and higher oligomers (where n is greater than 6-8 monomer units).
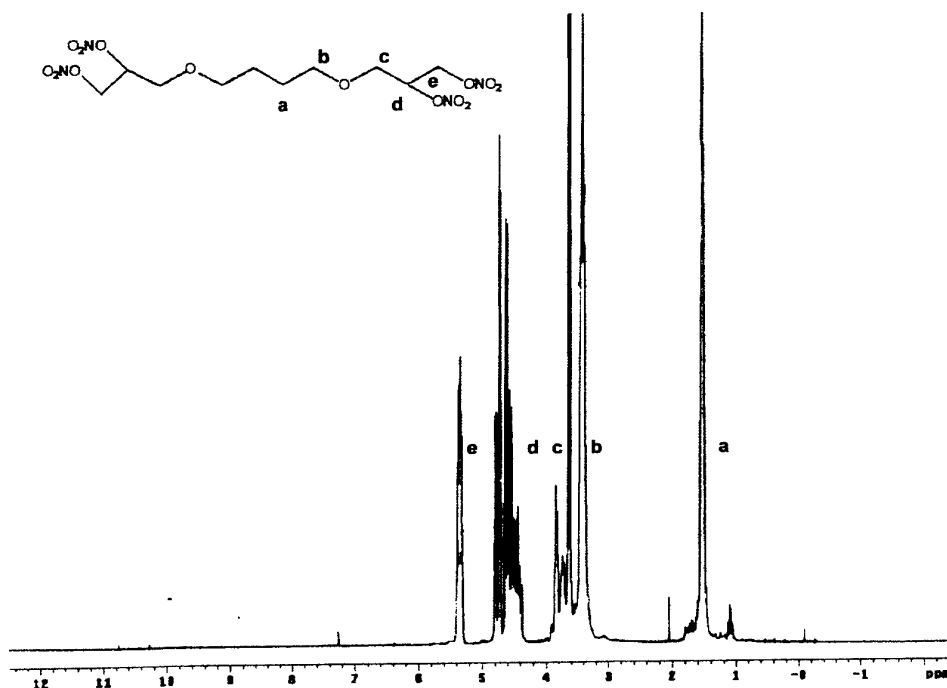

Figure 4: ¹H NMR Spectrum of GLYN Oligomer Plasticiser

In the proton and carbon NMR spectra (Figures 4 & 5), the GLYN oligomer can be characterised according to resonance **a** at 1.6 ppm (26.0 ppm; ^{13}C NMR spectra values in brackets) which belongs to the 1,4-butanediol methylene protons in the centre of the chain, the furthest protons away from the electronegative ether oxygen. Resonance **b** at 3.4 ppm (69.5 ppm) belongs to the methylene group of the butanediol chain nearest the ether oxygen, while resonance **c** at 3.6 ppm (67.0 ppm) is due to the methylene ether protons adjacent to the methylene nitroso groups. The C-H proton, **d** can be found at 4.8 ppm (78.0 ppm) and the methylene nitroso unit, **e** is found at 5.4 ppm (71.0 ppm). Impurities in the NMR spectra have not been fully identified.

Additionally, the final step of nitrating the plasticiser also affects final oligomer purity. In particular, nitration yields nitrated mono substituted butane and may possibly also produce nitroglycerine (not evidenced in NMR spectra). Nitration of the GLYN oligomer is not only necessary to give *explosophoric* nitrato groups but also to ensure that no hydroxyl species are present since the material will be used as a plasticiser in

plasticiser in isocyanate cured rubbers. Any hydroxyl moieties present will cure upon addition of isocyanate cure agents and lead to erroneous calculations of OH equivalent weight number.[1]
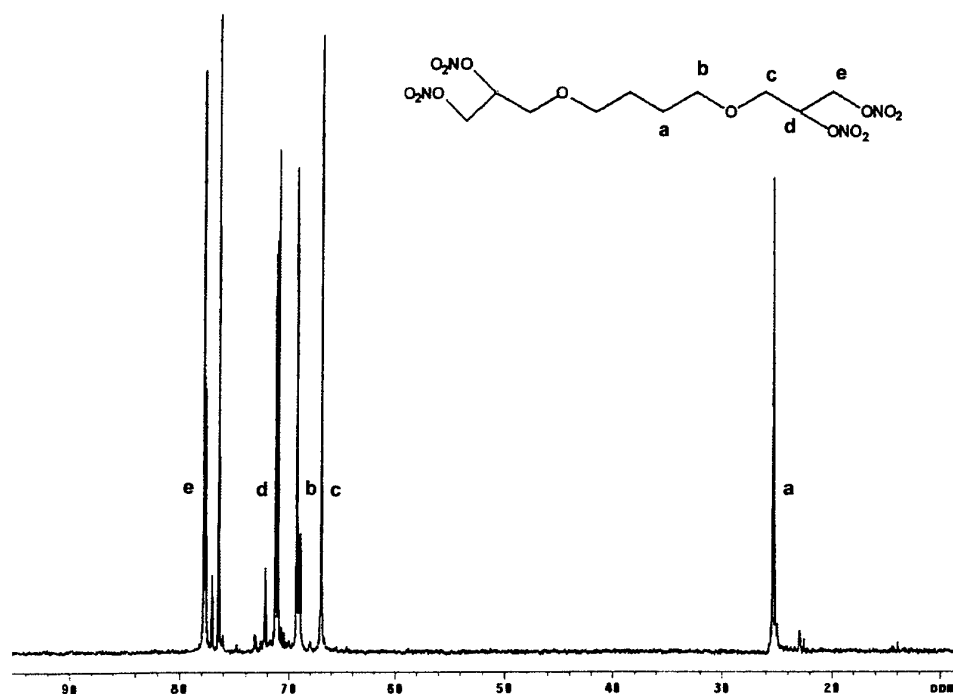
Figure 5: ^{13}C *NMR Spectrum of GLYN Oligomer Plasticiser*

4.1.4 Mass Spectral Analysis

The electrospray source mass spectrum of the GLYN oligomer gives charged sodium adducts as the major ion species (Figure 6). Two major peaks are evidenced, the molecular ion at m/z 441 which corresponds to sodiated GLYN oligomer, and a peak at m/z 560 which is essentially a sodiated trimer of the GLYN oligomer. A small peak at m/z 679 corresponds to the formation of a sodium tetramer of GLYN. Relative abundances indicate that the molecule comprises 80% of the oligomer species, with 16% contributing towards the trimer species followed finally by the tetramer species at 4% (Table 4).

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[1] The OH equivalent weight effectively means the amount of available hydroxyl groups for reaction with the isocyanate agents. It is commonly used to achieve desired cure properties.

Table 4:   Assignment of EI-MS Peaks of GLYN Oligomer

Assignment	Mol. formula	Calcd. m/z	Exptl. m/z	Error	Rel. abundance (%)
GLYN Oligomer	$C_{10}H_{18}N_4NaO_{14}^+$	441.26 (+Na$^+$)	441.07	1.26×10^{-6}	80.0
GLYN Trimer	$C_{13}H_{23}N_5NaO_{18}^+$	560.33 (+Na$^+$)	560.09	1.78×10^{-7}	16.0
GLYN Tetramer	$C_{16}H_{28}N_6NaO_{22}^+$	679.41 (+Na$^+$)	679.11	2.22×10^{-6}	4.0
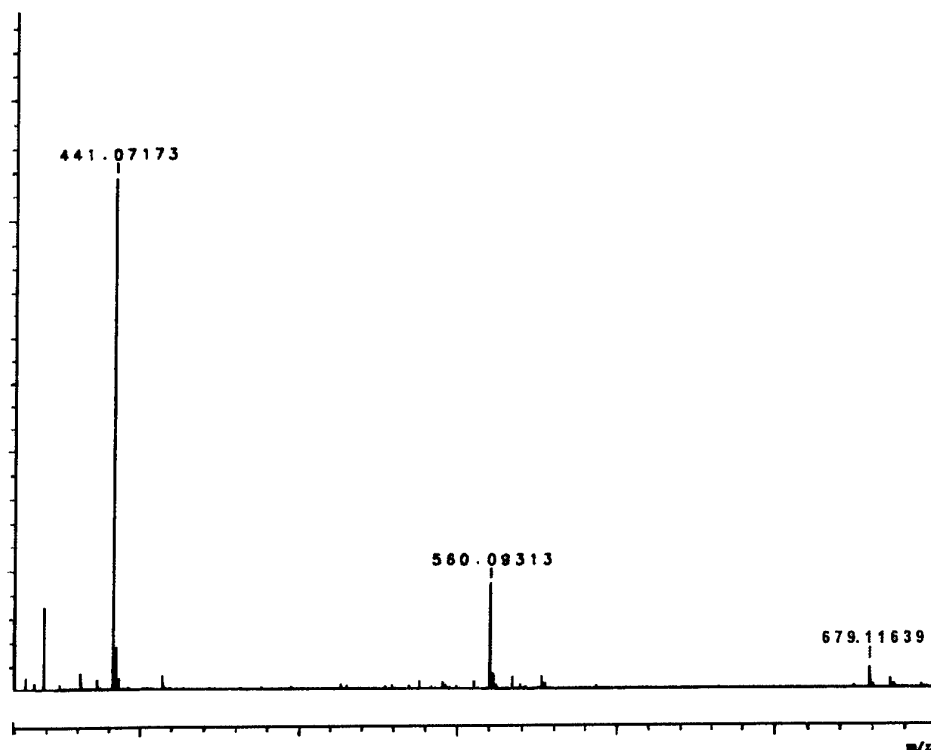
Figure 6:   Mass Spectrum of GLYN Oligomer Plasticiser

Figure 6 also shows the M–Na$^+$ fragment-adduct ions at m/z 418 for the GLYN oligomer and at m/z 537 for the trimer version. The M–Na$^+$ peak for the tetramer peak at m/z 679 is barely evident, a result of the low abundance of the tetramer. The presence of trimer and tetramer for energetic polyethers such as polyGLYN or polyNIMMO is consistent with observations by other mass spectra studies [10]. Kemp et al. [10] in particular, analysed polyNIMMO both prior to and after pyrolysis by MS and observed similar behaviour to that reported here for the GLYN oligomer.

Most literature reports focus on electron impact (EI) mass spectra of nitro compounds, and polyethers both of a cyclic [11] and acyclic nature [10], [12]. Consensus amongst the various papers is that monomer units are readily lost giving rise to product ions

and this is best described mechanistically by 1,4-hydrogen elimination with concurrent C–O bond cleavage. The bond cleavage step is often complicated by side groups, like the nitrato groups present in both polyNIMMO and polyGLYN.

It is quite likely that polyGLYN and the oligomeric GLYN undergo a similar mechanism whereby 1,4-hydrogen elimination with concurrent bond cleavage at the C–O bond occurs. The proposed mechanism is likely to take the form shown below and involves the loss of monomer units with 119 Daltons (m/z) (shown for polyGLYN):
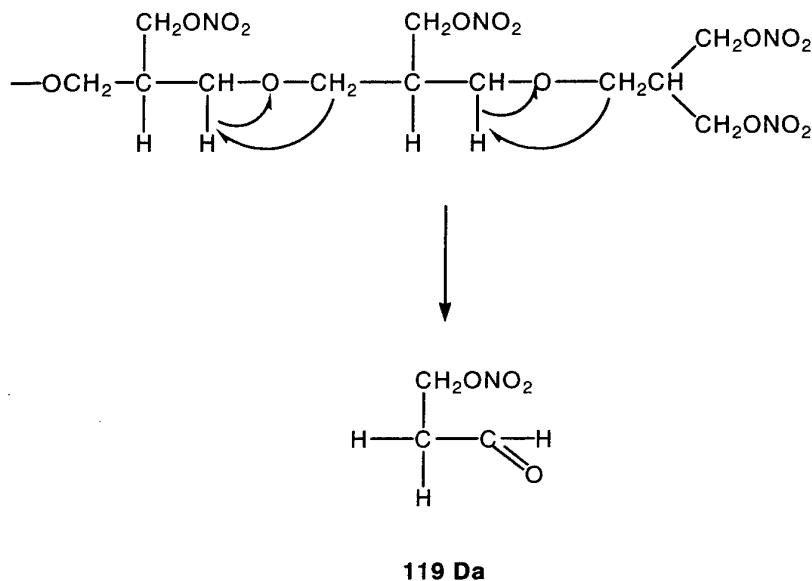
119 Da

Figure 7: Proposed Mechanism for Elimination of Monomer Unit from PolyGLYN of Mass 119 Daltons, i.e. the same as that of the repeat unit of polyGLYN

Kemp *et al.* [10] have conducted thermal degradation studies on polyNIMMO and pyrolysed polyNIMMO (140°C) and observed that polyNIMMO fragments typically at a loss of 30 Da during pyrolysis, with NO and CH_2O the two preferred species. Pyrolysis is known to result in chain scission and cross-linking of the polymer after 96 hr of pyrolysis. Similar behaviour where the nitro species was reformed after first cleaving a nitro group followed by elimination of formaldehyde has been observed by Kemp *et al.* [10]. Mass spectral analysis of the GLYN oligomer did not show the presence of such species.

Mass spectrometry confirms the structure of the plasticiser as well as indicating minor amounts of GLYN trimer and tetramer. Combined with the NMR spectroscopy information, which indicates the presence of several impurities, mass spectral information further allows us to more accurately elucidate the plasticiser structure.

4.1.5 Differential Scanning Calorimetry

The GLYN oligomer has been examined by differential scanning calorimetry to determine the Tg. DSC reveals a glass transition point of –55.2°C (Figure 8) and is in good agreement with [2].
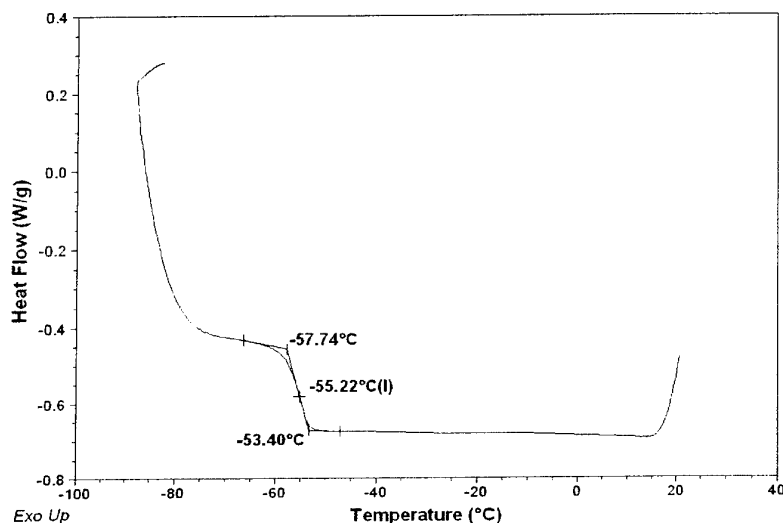
Figure 8: Sub-ambient DSC Trace of GLYN Oligomer

4.2 Sensitivity Testing

Small-scale hazard assessment data for the GLYN oligomer plasticiser is given in Table 5 and has a hazard rating of 1.3 (note that K10 is considered only as a Dangerous Goods Class 6.1). Rotter impact and electrostatic discharge were not measured as the required equipment was for testing of liquids. Interestingly, the manufacturer of the GLYN oligomer has obtained varying liquid height impact data ranging from 18.1 cm to between 8.2 and 10.1 cm [13]. Such variance indicates a certain sensitivity inherent in the plasticiser or may arise from differing impurity levels. For comparison, K10 plasticiser has a liquid height impact of 18.1 cm. Reconfirmation of this result would aid in proper hazard classification, however WSD does not at this present time have such a capability.

Table 5: Small-scale Hazard Assessment

Material	Liquid Impact Height, cm	T of I, °C
GLYN oligomer	10.1 [14]	183
K10	18.0 [13]	188

Temperature of ignition tests compared well with manufacturer specifications of 177 °C for the GLYN oligomer [14].

4.3 Compatibility Tests of Binder System

Unfilled plasticised binder systems were cured as fingers (Figure 3) and analysed for compatibility by vacuum stability tests and thermal analysis. Additionally, cross-link density determinations were carried out to gauge sol-gel properties. The soluble content of a cross-linked binder system is a useful tool for determining the extent of cross-linking. The greater the soluble content of non cross-linked binder, the higher the sol fraction.

4.3.1 Vacuum Stability and Hardness Tests

Vacuum stability tests were carried out at 100°C for 40 hr (Table 6) as testing of these materials at higher temperatures (120°C) results in excessive gassing. The acceptance criterion for thermal stability by this method is taken as less than 2 mL/g and is based on Test Series 7 of the United Nations' "Recommendations on the Transport of Dangerous Goods" [15]. All rubber formulations showed good stability when fully cured. Hardness tests were performed to gauge the relative strength of each formulation.

Table 6: Vacuum Stability and Hardness Testing of GLYN Oligomer Plasticiser and Unfilled PolyGLYN/GLYN Oligomer Binder Systems (at differing plasticiser % levels)

Binder System	Vac. Stab., mL/g	Hardness
Energetic Plasticisers		
GLYN oligomer	2.84, 3.05	N/D
K10	1.05 [2]	N/D
PolyGLYN/K10		
AP0402-01	1.2	31
AP0402-02	1.12	31
AP0402-03	1.09	18
AP0402-04	–	–
PolyGLYN/GLYN oligomer		
AP0402-05	0.78	18
AP0402-06	0.97	28
AP0402-07	0.92	14
AP0402-08	–	–

Vacuum stability results for the binders are low indicating good compatibility. The GLYN oligomer plasticiser has a high vacuum stability result, and was analysed a further time to confirm this high result. However, despite the GLYN oligomer's 'high'

gas volume, compatibility between the polyGLYN polymer and this plasticiser are still acceptable, falling below the acceptance criterion. It is well known that nitrate esters such as nitroglycerine (NG), evolve significant gas volumes upon vacuum stability testing as a result of the relative instability of the nitrate ester moiety [2]. Thus the GLYN oligomer plasticiser has an inherent instability due to the nitrate ester moiety accounting for the high vacuum stability test volume, rather than any incompatibility between the energetic binder components.

Additionally, when the GLYN oligomer plasticiser is incorporated into a polyGLYN matrix, lower vacuum stability volumes are obtained than for the K10 plasticised binders, indicating good compatibility between the GLYN oligomer plasticiser and polyGLYN polymer. Hardness values for the binders are highest at the 33% plasticised ratio for both K10 and GLYN oligomer. Plasticised loadings of over 50% of either plasticiser typically result in soft, tacky binder systems [2], with 67% plasticised systems failing to cure at all.

4.3.2 Thermal Stability Analysis

Thermal stability studies on the cured rubbers indicate low glass transition temperatures and relatively high decomposition temperatures implying good thermal stability suitable for use in munitions (Table 7).

Table 7: Thermal Properties of Rubbers

Binder System	Composition	Glass Transition Temperature, °C	Decomposition Temperature, °C
AP0402-00	100% PolyGLYN	– 31.5	204.3
AP0402-01	PolyGLYN; 25% K10	–29.6	211.3
AP0402-02	PolyGLYN; 33% K10	–37.2	209.7
AP0402-03	PolyGLYN; 50% K10	–45.3	208.0
AP0402-04	PolyGLYN; 66% K10	–	–
AP0402-05	PolyGLYN; 25% GLYN olig.	–29.8	205.3
AP0402-06	PolyGLYN; 33% GLYN olig.	–35.0	208.0
AP0402-07	PolyGLYN; 50% GLYN olig.	–40.7	205.2
AP0402-08	PolyGLYN; 67% GLYN olig.	–	–

If one is to consider the current UK operational requirement for the air carriage of munitions (ranging from –55°C to 71° [16]), then it is apparent from the above table that the energetic binders systems exhibit good thermal characteristics, possessing low glass transition points and relatively high decomposition temperatures. Such thermal stability makes these binders systems attractive for use in munitions such as ASRAAM.

4.3.3 Cross-link Density Determination

XLD have been determined for both K10 and GLYN oligomer plasticised binder systems and results presented in Table 8. Results indicate low amount of soluble

fraction for both plasticised systems with only minor variation between the plasticiser types.

Table 8: XLD Results for GLYN Oligomer and K10 Plasticised Binder Systems

Binder System	Weight fraction of Plasticiser	XLD
PolyGLYN/K10		
AP0402-01	25%	0.92
AP0402-02	33%	0.88
AP0402-03	50%	0.69
AP0402-04	67%	–

Binder System	Weight fraction of Plasticiser	XLD
PolyGLYN/GLYN olig.		
AP0402-05	25%	0.90
AP0402-06	33%	0.87
AP0402-07	50%	0.71
AP0402-08	67%	–

4.4 Determination of Plasticiser Efficiency

The experimentally determined glass transition temperatures can be described by mathematical equations, which relate the glass transition temperature (Tg) of a mixture to the Tg of the pure components [17]. Such mathematical models allow for the derivation of plasticiser efficiency and this can be used to compare between plasticisers and hence find required plasticiser loadings needed to obtain the required Tg.

Simple glass transition point theory for two component systems is based on two equations first derived by Gordon and Taylor [18]:

$$C_1(Tg\text{-}Tg_1) + \lambda C_2(Tg\text{-}Tg_2) = 0 \qquad (1)$$

Where $\quad C_1 =$ fraction of component 1
$\quad C_2 =$ fraction of component 2
$\quad Tg_1 =$ glass transition temperature of pure component 1
$\quad Tg_2 =$ glass transition temperature of pure component 2
$\quad Tg =$ glass transition temperature of the mixture

The λ term is obtained from:

$$\lambda = \Delta B_1 / \Delta B_2, \qquad (2)$$

where ΔB_1 is the difference in expansion coefficients for the rubbery and glassy states of component 1, etc.

Equation 3 is also known as the generalised Fox equation [19]:

$$1/Tg = 1/(C_1 + BC_2).(C_1/Tg_1 + BC_2/Tg_2) \quad (3)$$

where B is a constant dependent upon the plasticiser.

Both equations can be shown to be identical if we assume that:

$$\lambda = B.Tg_1/Tg_2 \quad (4)$$

Thus the slope λ can be obtained from a plot of $C_1(Tg-Tg_1)$ versus $C_2(Tg_2-Tg)$ and allows for the determination of B.

Typically, experimental data tend to have values of B greater than unity and thus the experimental points fall below this ideal line for simple theories. Deviations of the experimental data from a simple linear relationship are presented in Figures 9 and 10 for the two plasticiser systems tested. Gordon and Taylor define Tg by the amount of free volume changes of the glassy and rubbery states [18],[20]. The free volume is simply the incorporation of small molecules such as plasticisers expanding the polymer chain network. The plasticiser produces extra rotation of chain segments thereby increasing internal movement and reducing the Tg. The quantity B is related to free volume changes for glass transition temperatures that deviate from a linear relationship, the plasticiser is therefore causing a greater than ideal increase in free volume.

Correlating further, the plasticiser efficiency ε can be described as [17]:

$$\varepsilon = \lambda(Tg_1-Tg_2) \quad (5)$$

High plasticiser efficiency can be determined via two factors: 1) large variances in the glass transition temperature of the polymer and plasticiser and 2) large values of B or λ which represent the deviation of the plasticiser from ideal, linear behaviour. A summary of the data for polyGLYN with a wide variety of energetic plasticisers is presented in Table 9 and Figures 9 and 10.

Table 9: Plasticisation Efficiency for PolyGLYN

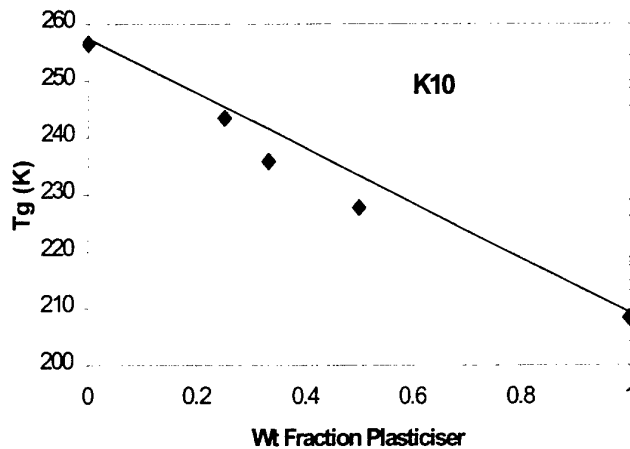| Plasticiser	Tg_1-Tg_2	λ	ε
GLYN oligomer	48.5	1.447	70.2
K10	48.2	1.387	66.8
BDNPA/F [2]	44.6	1.278	56.9
BuNENA [2]	64.2	2.029	130.3
MEN42 [2]	61.6	1.949	119.8
BTTN [2]	49.7	2.092	103.9
TMETN [2]	48.8	1.664	77.7

Figure 9: K10 Plasticised Binder Systems. Full Line Shows Calculated Linear Relationship
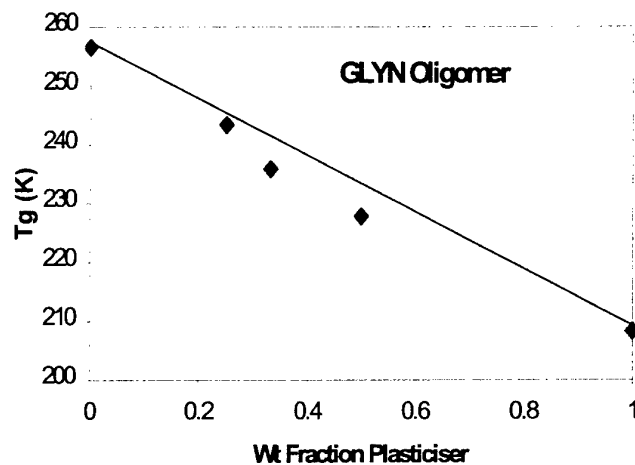
Figure 10: GLYN Oligomer Plasticised Binder Systems. Full Line Shows Calculated Linear Relationship

A general rule of plasticiser behaviour in a polymeric matrix is that the migration rate of a plasticiser through a binder matrix should follow an inverse correlation with molecular weight [2]. It is evident from Table 9 that the NENA plasticisers (BuNENA and MEN42) are superior to all other plasticisers, with high λ and ε values, however the NENA plasticisers are mobile and will exude from a PBX readily. This can be placed into context if we compare the molecular weights of each plasticiser; BuNENA has a molecular weight of 207 and MEN42 has a weight range from 165 to 179, the NENA plasticisers are relatively small when compared to the GLYN oligomer which has a molecular weight of 418. Both NENA plasticisers will exude out of a polyGLYN

matrix more readily than the GLYN oligomer. Comparing the GLYN oligomer plasticiser to the K10 plasticiser, the oligomer contributes towards a more efficient PBX by virtue of its higher plasticiser efficiency over K10, further evidence of the inverse correlation of plasticiser migration rates with molecular weight. Oligomeric analogues are thought to offer lower migration rates over plasticisers that have no structural similarity to the polymer and hence may find use in PBX systems since they confer a reduction in migration rates.

4.5 Diffusion Studies of GLYN Oligomer and K10 Plasticiser

Plasticiser migration is a common problem for most PBX formulations and use of the GLYN oligomer plasticiser is expected to have lower migration rates than K10 since it has a higher molecular weight (416 for GLYN oligomer c.f. 196 and 241 for dinitro- and trinitro-K10). To verify the inverse correlation of plasticiser migration rates with molecular weight, polyGLYN binder systems containing either 15% K10 or 15% GLYN oligomer plasticiser were analysed by isothermal TGA at 83°C, 99°C 115°C and 126°C under a nitrogen atmosphere. All runs show a decaying weight loss that approaches first order decay behaviour (Figure 11). Kinetic investigations into the decay rate constants, k, were determined via the slope of the linear regression plot and used to calculate diffusion coefficients, D (Table 10 and Figure 12). In addition, glass transition points for the 15% plasticised systems were determined, the GLYN oligomer having a Tg of –23.5°C and the K10 having a Tg of –19.5°C.

Table 10: K10 and GLYN Oligomer Plasticised Binder Diffusion and Rate Constant Values as Determined by Isothermal TGA.

Plasticiser	Temperature, °C	Time, min	k, s^{-1}	D, $cm^2 s^{-1}$
K10	83	4000	6.83×10^{-5}	7.76×10^{-7}
K10	99	4000	3.50×10^{-5}	3.97×10^{-7}
K10	115	4000	1.89×10^{-5}	2.08×10^{-7}
K10	126	4000	1.23×10^{-5}	1.39×10^{-7}
GLYN oligomer	83	4000	3.83×10^{-5}	4.35×10^{-7}
GLYN oligomer	99	4000	2.70×10^{-5}	3.52×10^{-7}
GLYN oligomer	115	4000	1.01×10^{-5}	1.14×10^{-7}
GLYN oligomer	126	4000	0.55×10^{-5}	5.68×10^{-8}

The activation energy, E_a or Arrhenius temperature dependence is obtained by a straight line from the plot of ln D versus 1/T (K) (Figure 12). For K10 plasticised binder systems, an activation energy of 114.8 kJ/mol was obtained while the GLYN oligomer has an activation energy of 112.6 kJ/mol. Coupled with the plasticising efficiency parameters calculated in the preceding section, the GLYN oligomer binder systems offer less exudation or mobility than K10.
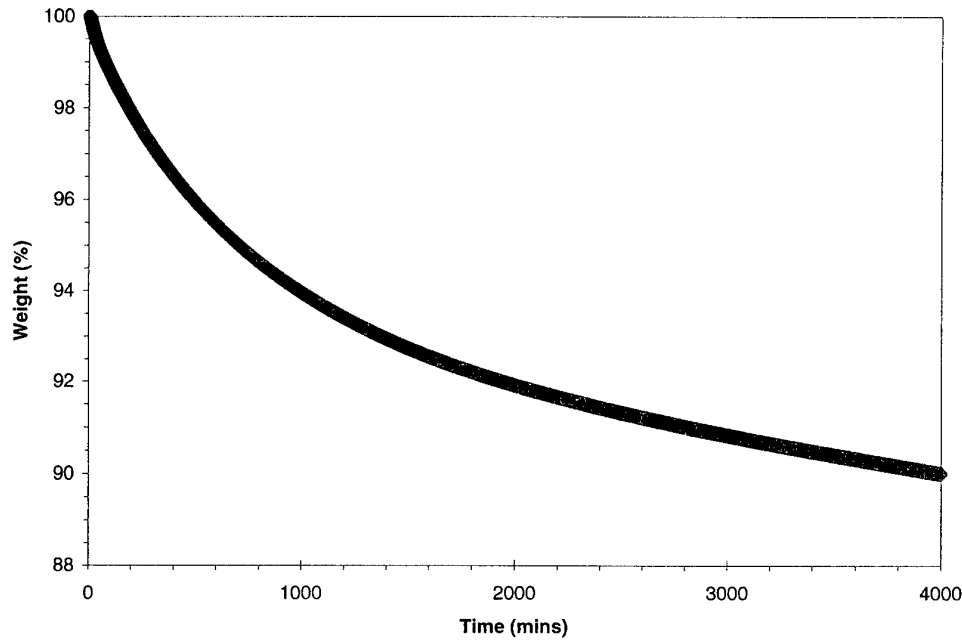
Figure 11: Isothermal TGA of 15% K10 in PolyGLYN Binder at 115°C
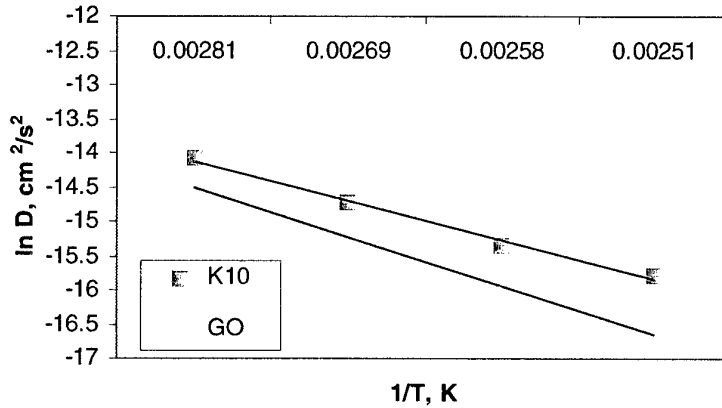
Figure 12: lnD vs 1/T Plot of 15% K10 and GLYN Oligomer in PolyGLYN Matrix. Line is least-squares best fit

Isothermal TGA experiments show that transport properties for both systems obey Fick's diffusion laws and allow for a reliable estimate of plasticiser migration. However several assumptions must be made, most importantly that plasticiser loss is the only source of weight variation. The binder system however, is a lightly cross-linked, amorphous structure that can undergo a variety of chemical reactions at higher temperatures, primarily degradation via thermolysis or chain cleavage. Thermolysis of similar nitrated polyethers such as polyNIMMO have been shown to have high

activation energies of 150-160 kJ/mol [21]. Furthermore, the lightly cross-linked network of polyGLYN should be expected to readily allow migration of small plasticiser molecules. Based on free volume theory, elastomeric materials such as the polyether systems like polyGLYN, should have high free volumes over polymers with highly cross-linked densities.

Kinetic investigations into plasticiser mobility gives activation energies comparable to literature reports, including Cartwright's migration of NENA energetic plasticisers (15% methyl, ethyl or butyl NENA in nitrocellulose binder) [3]. Activation energies for the NENA series ranged from 89 kJ/mol (BuNENA) to 120 kJ/mol (MeNENA), a result which also clearly demonstrates the molecular weight effect of the plasticisers on mobility through lightly cross-linked systems, with molecular weights for the NENA series ranging from 165, 179 and 207 for the methyl, ethyl and butyl variants, respectively. Activation energy results obtained for the GLYN oligomer, which has a nominal molecular weight of 418, is 112.6 kJ/mol, which is lower than that of the MeNENA and EtNENA activation energy values. However, the BuNENA shows lower activation energies than the GLYN oligomer and can be explained by variances in the techniques, including temperature differences between Cartwright's investigations (between 120°C and 130°C) to our technique of 105.7°C.

Further research conducted by Woolery *et al.* [22] on the thermal decomposition of polyGLYN at 110°C and 125°C also follows first order rate decay kinetics with an activation energy of approximately 125 kJ/mol, which is in keeping with our activation energy results of 112 kJ/mol and 114 kJ/mol for GLYN oligomer and K10 plasticised systems. Similar results for nitrocellulose (NC) and polyvinylnitrate (PVN), were obtained by Chen and Brill using pyrolysis-FT-IR [23] to give activation energies of 138 kJ/mol for NC and 133 kJ/mol for PVN. Differences in activation energy are likely due to variances in technique including heating rates, sample geometry and impurities.

4.5.1 Diffusion Theory

The evaporative rate of loss of a volatile liquid, according to diffusion theory, for a homogeneously distributed semi-infinite double-sided slab of thickness l, can be best approximated by [3],[24]:

$$W_t - W_e = \left(W_c - W_e\right)\left(\frac{8}{\pi^2}\right)e^{\left[-Dt\left(\frac{\pi}{l}\right)^2\right]} \tag{6}$$

Where W_t = volatile content of the solid at time t,

                W_c = initial volatile content,

                W_e = volatile content in equilibrium with environment,

                D = Diffusivity

Equation 6 is derived directly from Fick's second law of diffusion and assumes that D is independent of time and concentration and that the solid's thickness is small relative to its diameter. Thus equation 6 can be shown to have first order decay dependence

with time. Cartwright has shown that this holds true for NG migration from cross-linked double base propellants [3]. Resulting rate of weight loss for a first order fit is given by:

$$\ln\left[\frac{W_t - W_f}{W_i - W_f}\right] = -kt + c \qquad (7)$$

Where
W_t = Sample weight at time t,
W_f = Sample weight at infinite time,
W_i = initial sample weight,
k = first order rate constant
t = experiment time

Thus a plot of remaining plasticiser fraction versus time will be a straight line, with a slope equal to the first order decay constant, k.

Diffusion values for migration rates of plasticiser through a polymer matrix for a double sided slab of thickness l, can be obtained by:

$$D = k\left(\frac{l}{\pi}\right)^2 \qquad (8)$$

However we are using single sided theory, since the TGA pans allow for migration only from the top, while plasticiser migration from the bottom and sides of the alumina pan is prevented by interfacial bonding between binder and alumina pan. Thus, a single sided thickness (2l) equation is used:

$$D = k\left(\frac{2l}{\pi}\right)^2 \qquad (9)$$

Isothermal TGA experiments allows for a reliable estimate of plasticiser transport properties to migrate through a cross-linked polymer. GLYN oligomer plasticiser has been shown to have slightly slower migration rates over K10 and compares well to other energetic plasticisers such as MeNENA and EtNENA. However isothermal TGA is a technique which requires exhaustive use of the instrument, runs of the order of 4000 mins and generally take 3-4 days to complete. An alternative technique that allows for a more facile and less time consuming technique is still needed to address plasticiser migration, with pyrolysis connected to an FT-IR one possibility.

5. Conclusions and Recommendations

The energetic plasticiser, GLYN oligomer has been shown to reduce excessive exudation of plasticiser from the binder systems. Excessive plasticiser loss from a PBX matrix can lead to systems prone to sensitisation and subsequent degradation of IM properties. The use of a plasticiser that has a similar nature to the parent polymer of the binder system, allows for a more IM compliant munition as sensitivity effects are diminished.

Examination of the GLYN oligomer's plasticising properties has been conducted and shows good plasticiser behaviour compared to energetic plasticisers such as K10. More importantly, migration rates for the oligomer are lower than those for K10 plasticised binder systems as determined by isothermal TGA. Migration rates follow an inverse correlation with molecular weight and this has been shown to be the case for the oligomer over other energetic plasticisers. Additionally, compatibility testing by vacuum stability tests reveals better compatibility for the GLYN oligomer over the K10 energetic plasticiser in unfilled polyGLYN binder systems.

Sensitivity properties of the plasticiser have been measured and show good properties for inclusion into PBX systems. However, conjecture remains about the liquid impact height test results for the GLYN oligomer plasticiser. Verification of this test at our laboratory has not been conducted on the liquid plasticiser since WSD does not have the capacity for conducting such tests at the moment.

The performance of the oligomeric plasticiser in a PBX designed for metal accelerating roles forms the basis for another report, where PBX performance and sensitivity results for the GLYN oligomer plasticised PBX will be compared to K10 plasticised PBXs.

6. Acknowledgments

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Appendix A: Determination of the Soluble Fraction of the Energetic Binder

To measure the amount of crosslinking in an energetic binder system, the soluble content of the cross-linked polymer is required [25]. The greater the soluble content of non-crosslinked binder, the higher the fraction. Thus, the Charlesbey Pinner equation allows for the determination of the cross-link density, XLD provided the soluble fraction is known [26]. XLD is indirectly proportional to the soluble fraction.

$$XLD = \frac{(1-s)[2-(s+\sqrt{s})}{(s+\sqrt{s})} \qquad \text{(A1)}$$

s is the sol-gel fraction. A modified equation can be used whereby:

$$XLD = \frac{1}{\left(s+\sqrt{s}\right)} \qquad \text{(A2)}$$

The sol-gel fraction can be determined by extracting the soluble content of a polymer via Soxhlet extraction in dichloromethane.

Method

1. Extractions were carried out in duplicate.

2. Dry sintered glass thimbles (20 mm diameter) in a vacuum oven for three hours at 60 C, leave to cool for one hour in a desiccator.

3. Weigh thimbles to 4 significant figures (weight W_1, g).

4. Cut binder into cubes (1.0 mm X 2.0 mm X 2.0 mm) and place 1.0 g in the thimble.

5. Weigh thimble (weight W_2, g).

6. Using Soxhlet extraction apparatus, extract thimbles for 16 hours with 130 mL dichloromethane.

7. Remove thimble and place in fume cupboard and allow to air dry for 2 hours to evaporate excess solvent.

8. Evacuate residual dichloromethane in a vacuum oven at 60 C for 16 hours.

9. Place thimbles into vacuum desiccator containing dry silica and leave to cool for 1 hour.

10. Reweigh the thimble and sample (weight W_3, g) and calculate for sol percentage and then XLD.

11. Sol percentage can be calculated from:

$$\text{Sol} \% = \frac{(W_2 - W_3)}{(W_2 - W_1)} * 100$$

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4. AUTHOR(S) Arthur Provatas	5. CORPORATE AUTHOR Systems Sciences Laboratory PO Box 1500 Edinburgh South Australia 5111 Australia

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In an effort to comply with Insensitive Munitions (IM) criteria while minimising any reduction in performance, two part energetic binder systems which comprise an energetic polymer and an energetic plasticiser, are being developed for future use in PBX (polymer bonded explosive) fills in tactical missiles. Energetic binder systems confer energy output increases over conventional inert binder systems and are thus of interest to the ADF. Under a collaborative agreement with the UK, the ADF has received a new energetic plasticiser, GLYN oligomer, which promises to provide improvements such as higher energy output, good mechanical properties and low plasticiser exudation. This report serves to characterise the GLYN oligomer and examine its plasticising properties. Furthermore, comparison of migration data of the oligomer and other plasticiser(s) show that the GLYN oligomer is less likely to exude from PBX than other conventional plasticisers, thereby increasing the in-service life.