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Characterisation and Polymerisation Studies of Energetic Binders

Arthur Provatas

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ABSTRACT

In order to comply with Insensititive Munitions (IM) criteria, energetic binders comprising polymer and plasticiser(s) are finding use in cast-cured polymer bonded explosives and cast composite rocket propellants. Energetic binder systems confer energy output increases over conventional inert binder systems currently in use, and are thus of interest to the ADF. This report serves to characterise fully the physico-chemical properties of such energetic binder systems.

Both the uncured 'prepolymer' binder and the fully cured system have been characterised by various techniques including thermal analysis, spectroscopic analysis, sensitivity tests, molecular weight chromatography and mechanical properties. Detailed cure information obtained from these analyses are used to ensure effective cure.

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Executive Summary

The use of energetic binders (comprising energetic polymer and plasticisers), is driven by the need for more energetic yet more insensitive materials in modern IM (Insensitive Munitions) compliant munitions. Current polymer bonded explosives (PBXs) contain inert binder systems such as HTPB, and have limited explosive performance. Energetic binders alleviate this problem by confering additional energy to the munition, yet they also can offer improved insensitivity.

The energetic binders examined in this report are nitrato or azido functional polyethers such as poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO), poly(glycidyl nitrate) (polyGLYN) and glycidyl azide polymer (GAP). These energetic prepolymers are readily cured by means of urethane chemistry, whereby the hydroxyl terminated prepolymer is crosslinked with an isocyanate curing agent. This report serves to accurately characterise the physico-chemical properties of such energetic binder systems, which show promise as binders for advanced PBX's, and which will be utilised in DSTO's future energetic binder programs. Finally, a number of technical conclusions and recommendations for DSTO's future energetic binder program are made.

Authors

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Arthur Provatas graduated with a PhD (Chem. Tech.) from the University of South Australia in 1997 in polymer chemistry. During 1995, he interrupted his PhD studies to travel to the USA, as part of a joint Dow Corning-UniSA visiting fellowship to investigate advanced copolymeric materials made by interfacial polymerization. US patents have been awarded to this research. His multidisciplinary research has led him to publish research in inorganic chemistry, chemical engineering, polymer science, surface chemistry and organic synthesis. After a 6 month research attachment at the University, he commenced work for the Explosives Group of DSTO. The focus of his research at DSTO resides with energetic polymers as binders for military applications, polymer bonded explosives and energetic thermoplastic elastomers.

Contents

1. Introduction

Over the last 30 years catastrophic accidents involving stored munitions with violent response to unplanned stimuli, e.g. fire, bullet impact, adjacent detonation have become numerous. In an effort to reduce the severity of such accidents, the US Navy directed that all on-board munitions must be insensitive to hazardous stimuli. Such stores are known as insensitive munitions (IM). Various other countries, including Australia, have begun implementing similar IM programs introducing less sensitive munitions that have identical delivery parameters and terminal effects to their non-IM counterparts currently in service.

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 into IM by examining low sensitivity, polymer bonded explosive (PBX) based ordnance, containing energetic binders as a replacement for inert binders such as hydroxyl-terminated polybutadiene (HTPB). It is ultimately desirable that resultant munitions with comparable energy and reduced sensitivity over the current non-IM counterparts will find inventory with the ADF.

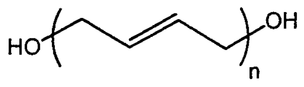
Research at DSTOs Weapons System Division is actively engaged in the development of new energetic formulations containing energetic binders. A binder, as its name implies, is a polymer that is used to bind together the separate ingredients of a formulation. The binder is cured by means of a curing agent leading to the formation of a three-dimensional network. Energetic binders examined in this report are nitrato or azide functional polyethers such as poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO), poly(glycidyl nitrate) (polyGLYN) and glycidyl azide polymer (GAP). These energetic polymers are readily cured by means of urethane chemistry, whereby the hydroxyl terminated polymer is reacted with an isocyanate curing agent to effect cure. Isocyanate cured binder systems have mechanical properties which depend strongly on the cure ratio of the isocyanate concentration to the hydroxyl concentration of the polymer.

2. Background

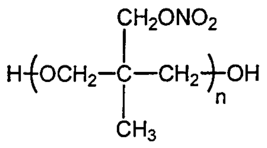
Current reduced-vulnerability explosives use cured binders systems that possess adequate dimensional stability and required energy absorbing properties but are ultimately difficult to recover or recycle either during manufacture or demilitarisation. One such binder, hydroxy-terminated polybutadiene, HTPB has excellent physical properties but is additionally an inert binder, that is the binder dilutes the overall energy output of the composition leading to a lowering of explosive performance characteristics.

Not surprisingly, this has brought a shift in direction from inert to energetic binders. Energetic binders contain energetic chemical groups known as *explosophores,* typically nitro (C-NO_2), nitramine (N-NO_2), difluoroamine (-NF_2), azido (N_3), and nitrate ester groups (-ONO_2). Such energetic binders impart to PBXs an increase in energy output, lower vulnerability and potential environmental benefits (incorporation of degradable functionalities in the polymeric backbone of energetic binders allows for the recovery and possible reuse of munition [2]). In addition, it is expected that these new energetic binders will lend themselves well to insensitive munitions, where a lowering of vulnerability with incorporation of an energetic binder occurs.

Three such polymers of interest to the Australian Defence Organisation are poly(3-nitratomethyl-3-methyloxetane), [PolyNIMMO], poly(glycidyl nitrate), [PolyGLYN] and glycidyl azide polymer (GAP), here shown with the inert HTPB.

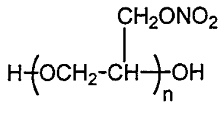


HTPB



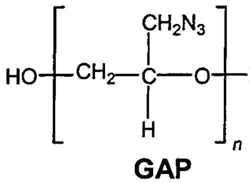
$$H\left(OCH_2-\underset{CH_3}{\overset{CH_2ONO_2}{C}}-CH_2\right)_n OH$$

PolyNIMMO



$$H\left(OCH_2-\overset{CH_2ONO_2}{CH}\right)_n OH$$

PolyGLYN



$$HO-\left[CH_2-\underset{H}{\overset{CH_2N_3}{C}}-O\right]_n-H$$

GAP

The characterisation of these energetic polymers is of importance to explosive chemists; knowledge and understanding of density, velocity of detonation, stability and compatibility, burning characteristics, degradation chemistry, side reactions and polymer morphology are all essential. Further aspects to be addressed are safety, suitability for service and useful service life.

The next generation of energetic binders therefore require accurate characterisation by analytical techniques to determine molecular weight, molecular weight distributions and functionality (amount of reactive functional groups per molecule), to allow optimization of the curing process. Common characterization techniques for energetic binders include nuclear magnetic resonance (NMR), infrared spectroscopy (IR), thermal analysis, density, and gel permeation chromatography, (GPC). NMR provides an analytical tool capable of determining functionality, polymer structure and quantitative analysis of end-groups. Thermal analysis provides pertinent information regarding the thermal history of the binder, including the decomposition point, melting behaviour and glass transition temperature, Tg (the temperature at which a binder undergoes a phase change from a glassy state to an amorphous state). Finally, GPC is used to elucidate molecular weight data including molecular weight distribution and average molecular weight.

This report aims to characterise various energetic polymers and their cured products by the techniques listed above. In addition, stability and sensitivity data have been collected on various cured polymer systems.

The following polymers were examined: di-functional polyNIMMO (PP670), tri-functional polyNIMMO (PP650), difunctional polyGLYN (batch number 21), two difunctional GAP polymers, XL GAP (a standard molecular weight range, M_n 2279 g/mol), and GAP LMW (a low molecular weight GAP variant, M_n 702 g/mol), and a branched GAP variant - B-GAP ($M_n \sim 4360$ g/mol). In addition, inert HTPB, has also been characterised to provide a benchmark reference to the energetic binders.

This report also details a study of two alternative Bayer isocyanate crosslinking agents - Desmodur N100 and N3400. It has been observed that curing of polyGLYN polymers with N100 and isophorone diisocyanate, IPDI produces brittle polymers with inadequate mechanical properties. In an attempt to produce polymers with improved mechanical properties, an alternative isocyanate (Desmodur N3400) has therefore been trialed. A series of polyGLYN formulations cured with either N100 or N3400 together with IPDI at differing ratios (25, 50, 75 & 100%) have been prepared and mechanically analysed for hardness and tensile strength.

2.1.1 NMR (Nuclear Magentic Resonance Spectroscopy)

NMR spectroscopy remains one of the most effective analytical tools available to binder chemists as it accurately elucidates structure and purity for both monomer and polymer, monitors cure reactions, and provides quantification of functional end-groups. Various NMR nuclei can be readily examined, with proton and carbon NMR (^1H and ^{13}C) the most frequently used techniques [3],[4].

For isocyanate curing reactions, one of the most common uses of ^1H NMR is when it is combined with FTIR (Fourier transform infrared spectroscopy) for the analysis of urethane formation during isocyanate cure [4]. NMR can thus be used to determine the completeness of the urethane reaction by the simple addition of trifluoroacetic anhydride (TFAA) to a sample of the polymerization mixture with deuterated chloroform. The acid reacts with alcohols that have not yet formed urethane linkages to form fluoroether end groups, allowing facile identification and quantification of urethane end-groups (by comparison of shifts both pre and post TFAA treatment). The reaction is also easily monitored by FTIR, where quantification of the carbonyl vibrations of reactant isocyanate and post reactant urethane groups are analysed by infrared spectroscopy.

2.1.2 End-Group Determination

Most polymers contain terminated free hydroxyl groups, and it is these groups that determine the functionality number needed to accurately assess polymerization conditions. Functionality is defined as the average number of OH groups per polymeric chain [5]. The functionality of hydroxyl groups influences the structure of the polymer - directly affecting the modulus, stress and strain capabilities of cured formulations and is therefore an important parameter that requires accurate determination.

To determine functionality, end-group analysis is required and can be performed using several techniques including titration (least accurate technique), acetylation techniques (catalysed with 2-methylimidazole), infrared spectroscopy, gelation and NMR spectroscopy techniques. The gelation technique, as pioneered by Oberth, involves measuring the time for isocyanate polymers and triol crosslinkers to gel and is considered to be the most reliable method for determining hydroxyl functionality although it is a time consuming process [6]. In the case of NMR, the reaction of free hydroxyl groups with trifluoroacetic anhydride or hexafluoroacetone is determined by measuring the integral (by ^{1}H NMR) of the α-methylene protons versus an internal standard [7]. ^{13}Carbon NMR is also particularly useful for investigating polymer end groups, since it is often possible to predict the expected chemical shifts accurately for different end group structures from the main chain shifts. Following initial studies by Grant and Paul [8] and Lindeman and Adams [9] for hydrocarbons, it is now possible to predict ^{13}C NMR chemical shifts by simple additive schemes, and this has since been extended to include many atoms and functional groups.

Another spectroscopic technique, near-infrared spectroscopy NIR, can also be used to measure the hydroxyl number [10]. The technique measures the adsorption of near infrared radiation (14 000 to 4000 cm^{-1}) of organic molecules, offering a quick, non-destructive technique for measuring hydroxyl number without any sample preparation. The use of NIR spectroscopy has now grown dramatically with the advent of high powered computers making this technique facile and accurate.

2.1.3 Molecular Weight

Second only to polymer composition, the parameters of greatest influence on the physical properties of energetic polymers are the average molecular weight and molecular weight distribution. These parameters are readily measured by gel permeation chromatography, GPC, vapour phase osmometry or light scattering techniques. Typically, GPC finds the most use for determining molecular weight, although light scattering techniques, in particular low angle laser light scattering, LALLS, are becoming more prevalent.

The separation of components in a polymer by GPC is a result of steric exclusion of the polymer molecule or a difference in molecular size in solution, where the larger molecules are found in the early elution volume [11]. The molecular size (or hydrodynamic radius) of a polymer component depends upon molecular weight, chemical composition, molecular structure and experimental parameters (solvent, temperature and pressure) and requires accurate calibration by GPC polymer standards. Often an appropriate standard is unavailable, as is the case for new energetic materials, and this may cause incorrect molecular weight calculations. Use of LALLS in combination with a concentration detector (refractive index, IR or UV) allows for the measurement of accurate molecular weight without relying upon calibration standards. LALLS has been applied to energetic polymers such as the oxetanes and azido functionalized polymers [12].

3. Experimental

3.1 Materials

HTPB, grade R45HT, is produced by Atochem Inc., USA and was obtained through Australian agents Elf Atochem (Aust.). PolyNIMMO PP670 and PP650 (di-functional and tri-functional polymers, respectively) and polyGLYN (batch BX-21) were purchased from ICI Nobel Enterprises (Ardeer, Scotland) and degassed prior to use. XLGAP, GAP LMW and B-GAP were obtained from 3M, USA 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 & N3400, both polyfunctional isocyanates (functionality of 2.3 and 2.7, respectively), were also obtained from Bayer and used as received. Dibutyl tin dilaurate (DBDTL) is a cure-accelerating catalyst obtained from Aldrich and was 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 generally 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) analysis was performed using a Perkin Elmer Pyris 1 under nitrogen purge in closed aluminium pans. Glass transition temperatures (Tg) were carried out by cooling sample to -120°C for 1 minute and then heating to 0°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. A simultaneous TGA-DTA thermogravimetric analyser coupled with a DT100 datataker was used to measure weight loss over the temperature range 25 to 400°C at 10°C per minute. All samples were run under an air atmosphere at a flow rate of 50 mm/min.

Gel Permeation Chromatography (GPC) was used to determine molecular weights and conducted on a Waters 2960 GPC with refractive index detector. The column set comprised 10^3 and 10^4 Å Ultrastyrogel columns (Waters). Sample concentrations were accurately weighted in toluene and 10 μL injected into the GPC. THF, the mobile phase eluent, was purified by filtering chromatographic grade THF (Crown Scientific) through a 0.45 μm nylon membrane and degassing prior to use. Standardisation of the GPC was accomplished by use of polystyrene standards of known molecular weight (Waters). The standards were made to a 10% wt/wt solution in toluene and 10 μL injected into the GPC.

Absolute densities were determined using a Quantachrome Helium Ultrapycnometer 1000 by the procedure given in test 1 (absolute density determination) of [13]. 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

The following isocyanate cured rubbers were made to assess vacuum stability, thermal properties (glass transition point and decomposition behaviour) and mechanical properties (tensile strength and hardness). All formulations were hand mixed in a glass beaker. An isocyanate to hydroxyl group ratio of 1.1 : 1 was used with 5 ppm DBDTL cure-accelerating catalyst. ICI recommends a 50:50 isocyanate mixture of N100/IPDI for polyGLYN [14] and this recommendation was employed for all formulations. For polyNIMMO, ICI recommends employing 100% N100, and this amount was subsequently used in polyNIMMO formulations.

Binder formulations were prepared by first degassing polymer in vacuum oven at 70°C for 16 hours. The binder was then mixed in a glass beaker with isocyanate plus catalyst until homogeneous and then degassed for 1 h at 70°C under vacuum. The binder was then cast into Teflon moulds (11.0 cm × 6.0 cm × 1.5 cm) and degassed at 70°C under vacuum until gas evolution ceases. The vacuum was released and binder left to cure at 70°C for 7 days.

Table 1: Formulation Data for Rubber Compositions (38 to 43E). All formulations contain 5 ppm dibutyl tin dilaurate as catalyst.*

Formulation	Ingredients	Wt, %	Appearance
38	HTPB R45HT	75	Dark yellow
	Desmodur N100	12.1	
	IPDI	12.9	
39E*	Di-polyNIMMO	81.4	Pale yellow
	Desmodur N100	17.6	
40E	Tri-polyNIMMO	90.2	Pale yellow
	Desmodur N100	9.8	
41E	PolyGLYN#21	90	Yellow
	Desmodur N100	4.7	
	IPDI	5.8	
42E	XL GAP	91.5	Yellow
	Desmodur N100	3.9	
	IPDI	4.6	
43E	Branched GAP	83.5	Straw yellow
	Desmodur N100	7.6	
	IPDI	8.9	

* E = energetic binder

3.4 Hazards and Mechanical Properties Testing

3.4.1 Rotter Impact Sensitiveness

Impact sensitiveness was determined on a Rotter apparatus [15]. Samples were prepared from cast-cured sheets of material under investigation using a scalpel to cut individual discs each of about 30 mg. Each sample was then placed in a brass cap, allowed to stand overnight in a dessiccator, then fitted over a polished steel anvil and impacted by a 5 kg weight falling from a preset height.

Go/no go was determined by the evolution of gas, a positive result being recorded for >1 mL. Impact height was varied in a typical Bruceton procedure with a total of 50 caps being tested.

The resulting figure of insensitiveness (F of I) is quoted relative to RDX, Grade F = 80 and is rounded to the nearest 5 units. Gas evolution represents the average of all positive results.

3.4.2 Friction - BAM Test

The BAM test measures friction values by applying a thin film of sample to a ceramic tile and lowering the friction apparatus arm. The heaviest weight was placed on the outer groove of the arm and the button on the machine pressed, dragging the ceramic pellet across the sample. The sample was observed for any sign of ignition, spark or smoke and repeated with weights of decreasing mass until six repetitions with the same weight provide no evidence of ignition. This weight is reported as the minimum required for ignition.

3.4.3 Temperature of Ignition

Temperature of ignition (T of I) was determined on an instrument built to specification for the ERDE T of I test [15]. 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 this event occurs.

3.4.4 Electrostatic Discharge, ESD

This test is performed according to the UK Sensitiveness Collaboration Committee 'Manual of Tests'. The five cavities in the polyethylene strip were filled with the sample. Cover each hole individually with a small square of copper foil. Place the strip on a brass platform that is connected to one side of a non-inductive capacitor. Arrange a second brass terminal, connected to the other side of the capacitor, to touch the first of the small pieces of foil on top of the polyethylene strip.

A capacitor of 0.1 mF, 0.01 mF or 0.001 mF is selected using a switch that will connect to earth. The capacitor is charged to a potential of 9.5 kV, giving a stored energy of 4.5 J, 0.45 J or 0.045 J, respectively. The test is initiated by applying a pulse that causes the potential of the selected capacitor to form across the sample spark gap.

3.4.5 Vacuum Stability

Duplicate 2.0 g samples of the formulations were placed in glass sample tubes which were then attached to a mercury-filled manometer and evacuated [16]. 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 the average of duplicate samples.

3.4.6 Hardness

The ASTM-D2240 method was used to assess Shore "A" hardness [17]. 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 center to edge were found to be insignificant for respective surfaces. Five indentations per assessment were performed at ambient room temperature.

4. Results and Discussion

4.1 Polymer Characterisation

Hydroxyl-terminated polymers like polyNIMMO, polyGYLN and GAP need to be accurately characterised by spectroscopic and chromatographic techniques to determine chemical structure information, OH equivalent weight numbers, molecular weights and functionality. Typical characterisation issues encountered include: (1) variation in results by different analytical methods, (2) large sample size, (3) poor reproducibility, and (4) difficulty in applying standard analytical methods to various polymers as a result of the differences in chemical structure. Nevertheless characterisation serves as an important consideration for future scale-up work and for optimisation of polymerisation processes.

Polymer characterisation included IR analysis, density measurements, NMR (both ^{1}H and ^{13}C), thermal analysis and GPC. A combination of titrimetric methods and NMR spectroscopy allows for the determination of equivalent weight numbers, which are essential for determining functionality. The functionality of a polymer allows for an estimate of crosslinker that is required for polymerisation.

Infrared Analysis

Initially, polymers GAP, polyNIMMO and polyGLYN were characterised by IR to ascertain functional group absorbance bands (Table 2). All absorbances correspond to those of literature sources. There is no discernible difference between di- and tri-functional polyNIMMO IR absorbances and between XL-GAP, GAP LMW and B-GAP absorbances. For GAP polymers, the azido group is observed at 2105 cm^{-1}, while for polyGLYN and polyNIMMO polymers, the nitrato group absorbances are observed at 1640 and 1280 cm^{-1}.

Table 2: IR Absorbances for GAP, PolyNIMMO and PolyGLYN

Polymer	Wavenumber, ν, cm^{-1}	Assignment	Intensity*
GAP	3470, 3360	N-H/ O-H	br
	2940, 2880	C-H	s
	2105	N_3	s
	1445	C-H	m
	1100	C-O	s
PolyNIMMO	3440	O-H	w
	2960	C-H	m
	1640	ONO_2	s
	1455	C-H	m
	1370	NO_2	m
	1280	ONO_2	s
	1100	C-O	s
PolyGLYN	3450	O-H	m
	2890	C-H	s
	1640	ONO_2	s
	1460	C-H	m
	1390	NO_2	m
	1280	ONO_2	s
	1100	C-O	s

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

Density

Relative density measurements have been recorded by a Helium Ultrapycnometer and results displayed in Table 3. Interestingly, property-structure relationships between the polyethers - polyNIMMO and polyGLYN, show that the polymer polyGLYN has a higher density than polyNIMMO (1.41 vs 1.25 g/cm^3). Coupled with this higher density for polyGLYN is its higher energy output than polyNIMMO (2661 kJ kg^{-1} [$\Delta H_{expl.}$ (calc.)] versus 818 kJ kg^{-1}) [18]. Such increased density and energy output have made polyGLYN the favoured candidate in energetic binder systems in comparison to either GAP or polyNIMMO. However it must be stressed that energy is not the only factor required, quite often safety and sensitivity issues (as in the case of IM compliance) are of paramount importance, and may necessitate the use of less energetic polymers such as polyNIMMO.

Table 3: Relative Density of Polymers

Polymer	Measured Density, g/cm^3	Literature Density, g/cm^3
HTPB R45HT	0.87	0.95 [19]
PolyNIMMO PP670 (difunctional)	1.25	1.26 [19]
PolyNIMMO PP650 (trifunctional)	1.21	1.26
PolyGLYN#21	1.41	1.45 [20]
XLGAP	1.27	1.30 [19]
GAP LMW	1.26	1.30
Branched GAP	1.24	1.30 [21]

NMR Spectroscopy

Nuclear Magnetic Resonance spectroscopy allows for complete characterisation of the polymers including structure and purity determination. Figures 1 and 2 show representative ^{1}H NMR spectra of polyNIMMO and polyGLYN. PolyNIMMO is soluble in deuterated chloroform while polyGLYN is soluble in deuterated acetone. All of the resonances have been correctly assigned and are in accordance with manufacturers spectral characterisation for both proton and carbon nuclei.

In the proton NMR, polyNIMMO is characterised by 4 main resonances, which are shown in Figure 1. Resonance **a** at 0.9 ppm is due to the methyl group, resonance **b** at 3.25 ppm belongs to the methylene ether protons ($-OCH_2-$). Resonance **c** at 4.4 ppm is due to the methylene protons on the methylene nitroso unit and the final peak resonance **d** at 2.1 ppm belongs to the terminated hydroxyl functionalities.

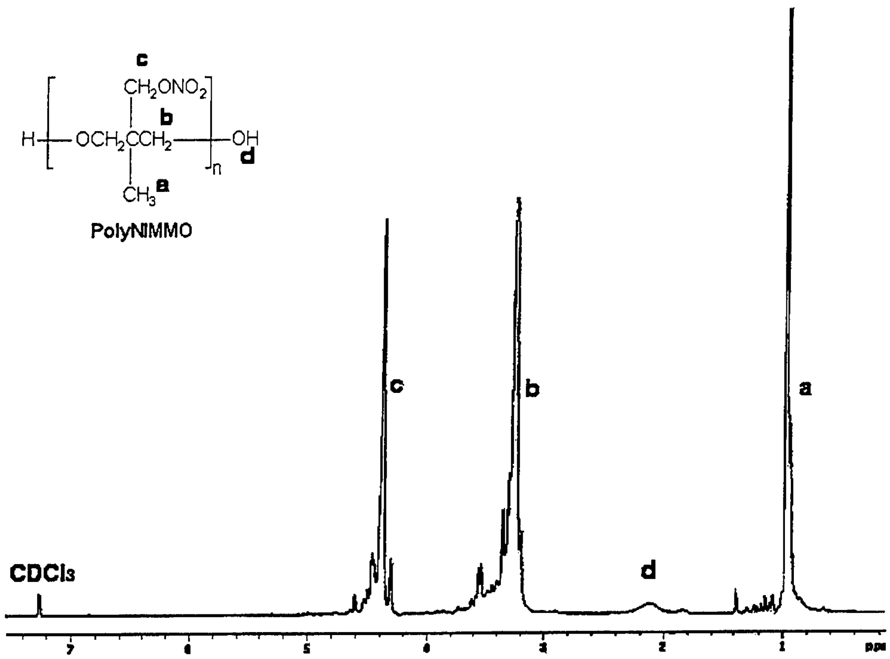


Figure 1: ^{1}H NMR Spectrum of PolyNIMMO (Trifunctional).

PolyGLYN, similar in structure to polyNIMMO, displays similar resonances; resonance **a** at 3.6 ppm is due to the methylene protons on the methylene ether protons while resonance **b** at 1.55 ppm is due to the C-H proton at the chiral center (Figure 2). Resonance **c** at 4.5 ppm is due to the methylene nitroso unit and the broad resonance **d** at 2.9 ppm is due to the terminated-hydroxyl functionalities. Resonances at 1.1 and 5.3 ppm are due to any unremoved initiator (tetrafluoroboric etherate) [20].

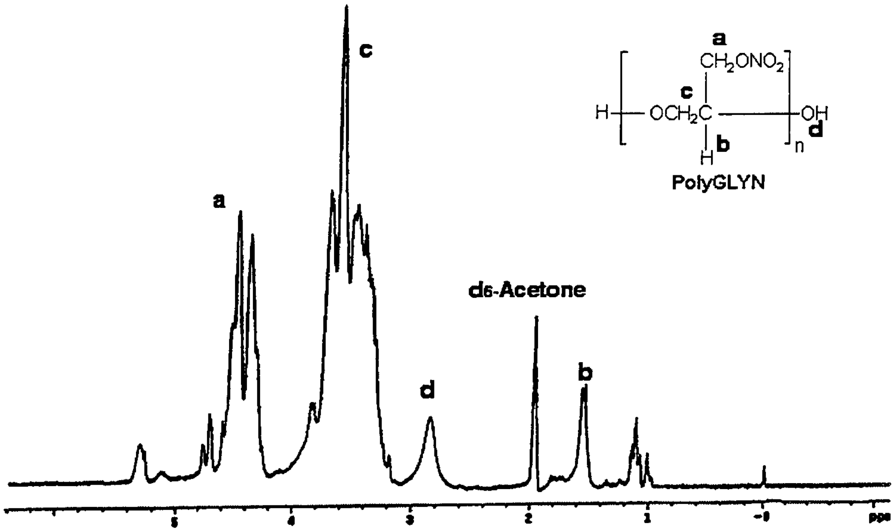


Figure 2: ^{1}H NMR Spectrum of PolyGLYN

Other information obtainable from NMR includes the determination of polybutadiene microstructure (cis, trans and vinyl content) for diene containing polymers such as HTPB [22]. For polybutadienes, the vinyl content is given by:

$$\text{Vinyl Content} = \frac{A+B}{(A+B+C)} * 100\% \qquad (1)$$

Where **A** is the area of the vinyl CH peak, **B** the vinyl CH_2 peak and the *cis* and *trans* peaks, **C** [22]. HTPB RT45 has been found to have a vinyl content of 91.6% by measurement of ^{13}C NMR employing a suitable relaxation agent (chromium acetylacetonate) and pulse sequence to eliminate relaxation effects (Figure 3).

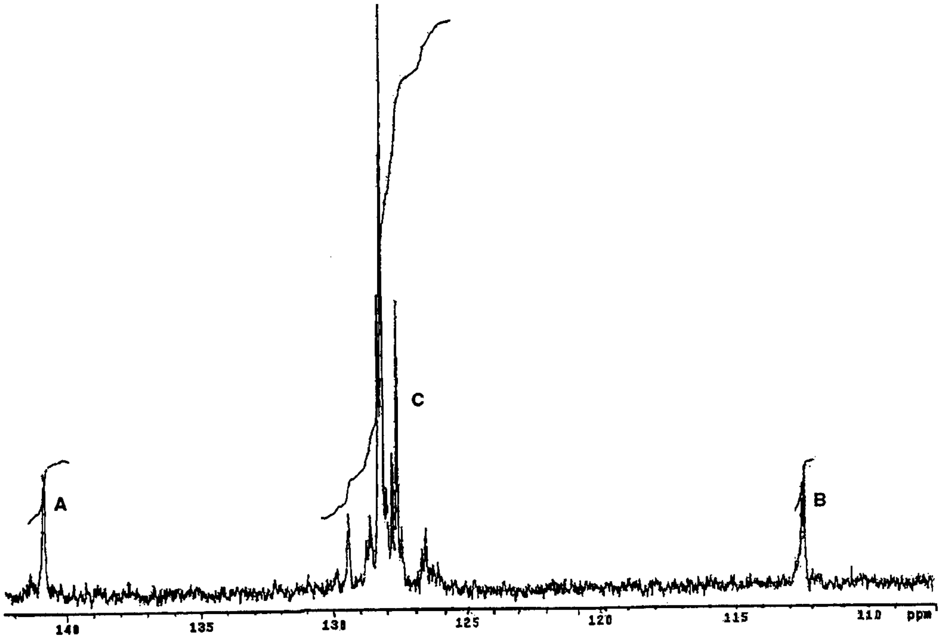


Figure 3: ^{13}C NMR Spectrum of HTPB

Gel-Permeation Chromatography
Molecular weight data for all of the polymers have been evaluated by GPC and are shown in Table 4. Most experimental values are comparatively close to reference data (if available), indicating well defined narrow molecular weight distribution polymers.

Table 4: GPC Results for Polymers

Polymer	M_n[a]	M_w[b]	Polydispersity, PD (M_w/M_n)	Reference
PolyNIMMO PP670 (difunctional)	1888	3637	1.93	M_w 3186 M_n 1669, PD 1.91 [23]
PolyNIMMO PP650 (trifunctional)	1601	2896	1.81	M_w 2375 M_n 1445, PD 1.64 [23]
PolyGLYN#21	1964	4385	2.21	M_n 1100-2000 M_w 2000-3500 [23]
GAP LMW	702	1159	1.65	No data
GAP XL	2279	5426	2.38	No data
B-GAP	1440	5058	3.50	M_n 4360 (polystyrene) [21]
HTPB R45HT	2291	4028	1.75	M_w 2800 [24]

[a] molecular weight based on the number average
[b] molecular weight based on the weight average

M_n, the number average molecular weight, is the ratio of the total weight of the sample to the total number of molecules present. On the other hand, M_w, the weight average molecular weight, is the mean value of the weight distribution of molecular sizes. Understandably, M_n is the more commonly used molecular weight average being the most easily measured. However, M_n is sensitive to low molecular weight species as they contribute markedly to the number of molecules present than to weight. Compared to M_n, small amounts of high molecular weight polymer contribute largely to M_w, while low molecular weight species contribute little.

Polydispersity is simply M_w/M_n, and relates to the distribution of molecular sizes in a polydisperse polymer (most polymerisation routes are random in nature and lead to polydisperse polymers). A polydispersity close to 1 indicates a polymer having a well-defined narrow molecular weight distribution. For comparison, branched GAP has a polydispersity of 3.50 due to its highly branched structure. There is also a large discrepancy between the reference molecular weight number of B-GAP and the measured, and this may be attributed to the GPC standards used to measure M_n (both analyses use polysytrene standards, however variancies may occur) or analytical error.

Thermal Analysis

Thermal properties of the polymer have been measured by DSC and TGA and are displayed in Table 5. All values are averages of two measurements. The Tg was taken as the point of inflection of the specific heats for the glass and rubber phases of the polymer. High temperature decomposition behaviour is measured by heating in DSC from 25 to 500°C at 5°C per minute.

TGA was used to assess weight losses over the temperature range 25 to 400°C at 10°C per minute and was run under an air atmosphere at a flow rate of 50mm/min. TGA results are given in weight loss percentage at 130°C.

Table 5: Thermal Properties of Polymers (where known, reference values are given in brackets, literature references in square brackets)

Formulation	DSC		TGA
	Tg, °C	Decomp., °C	Weight loss, % @ 130°C
PolyNIMMO PP670	-30 (-26, [21])	220 (216, [21])	8.2
PolyNIMMO PP650	-30 (-26, [21])	219 (216, [21])	3.2
PolyGLYN#21	-32 (-35, [25])	210 (222, [25])	5.9
GAP XL	-46 (-40, [25])	220 (212, [25]	12.2
GAP LMW	-44	222	10.9
Branched GAP	-38 (-36, [21])	250 (252, [21])	11.8
HTPB R45HT	-83 (-66, [19])	450	1.2

Using TGA at 130°C (temperature at which sample can be considered as moisture free and hence, a more representative sample), all polymers display low weight loss implying inherent stability of the polymer. The GAP polymers display the highest percentage of weight loss in comparison to polyNIMMO and polyGLYN. DSC measurements reveal low glass transition points for all polymers and relatively high decomposition points with good comparison to reference literature sources. The most thermally stable polymer is the inert HTPB, a result which is expected given HTPB's predominantly linear structure with minor branching (1,2-addition), which allows for a larger degree of freedom of rotation in the polymeric backbone and hence more thermal stability. PolyGLYN and polyNIMMO on the other hand, incorporate heteroatoms, functional groups such as the nitrato and ether linkages and steric crowding, all of which contribute to larger amounts of steric hindrance, forcing the molecular freedom of rotation to be reduced and thus a reduction in thermal stability.

4.1.1 Equivalent Weight/Functionality Analysis of Polymers

Chemical and physical properties of cured energetic polymers depend on the amount and type of hydroxyl species present in the polymer. Thus, the hydroxyl concentration of energetic polymers is often expressed as the hydroxyl equivalent weight (commonly abbreviated to OHV, OH Value) and is defined as the ratio of the number average molecular weight of the polymer and its hydroxyl functionality. Functionality is defined as the average number of OH groups per polymeric chain. Since the formation of the polymer is of a statistically random nature, not all polymer chains have the desired end groups. As a result, polymers have a distribution of functionality and their hydroxyl equivalent weight has to be determined by chemical or physical methods. Accurate and reliable OH equivalent weight numbers are important, since the functionality and amount of isocyanate required for cure reaction to form a favourable elastomeric network are based on the hydroxyl equivalent number.

Methods to ascertain the concentration of hydroxyl groups include titrametric methods (acylation by acetic anhydride or acetyl chloride catalysed by pyridine, imidazole or boron trifluoride) [26] and infrared spectroscopy methods (direct measurement by various techniques such as FT-IR or NIR (near-infrared spectroscopy), or via deuterium exchange) [27]. These methods suffer from the presence of water or various other factors such as the need for large quantities as well as being time consuming. The hydroxyl equivalent weight can also be determined by nuclear magnetic resonance (NMR), where the polymer is first derivatised with trifluoroacetic anhydride [7, 28]. NMR methods are fast and require a small amount of polymer, however they suffer from reactivity (different chemical methods may give differing values of equivalent weight depending on polymer type).

The titration and NMR methods involve an acetylation reaction of the polymer while the IR method requires a calibration curve. The former methods suffer if the acetylation reaction is not allowed to go to completion, while the latter method suffers predominantly from moisture contamination.

The energetic polymers discussed within this report have had their equivalent weights determined by both titrametric and NMR spectroscopic methods. Results are presented in Table 6. NMR analysis generally gives a more accurate picture of determining equivalent weight numbers over the titrametric method, although this is not supported in the value obtained for polyGLYN. This may be attributed to the chiral center in the polyGLYN polymer which gives rise to broad peaks in the NMR spectrum [29].

The OH equivalent weight numbers were first measured by a titrimetric method proposed by Manzara of 3M [30], based on *N*-methylimidazole for GAP polymers (see Appendix A for technical procedure). Polymers of most interest (polyGLYN, polyNIMMO) and HTPB were then analysed for equivalent weight numbers by NMR based on [31],[32] and [33]. The NMR technique for such analyses is provided in Appendix B.

Table 6: Polymer Hydroxyl Equivalent Weight Numbers and Functionality (in brackets).

Polymer	OH Eq. Wt. Methods[a]		Reported Values
	Titrametric	NMR	
Poly NIMMO PP670	2710 (20.7)	1821.8 (30.8)	1402.5–3085.5 (40–18.2) [23][b]
PolyGLYN#21	930.9 (60.2)	1048 (54.1)	958 (58.6) [23][b]
GAP LMW	996.8 (56.3)	N/D	-
GAP XL	4381 (12.8)	N/D	-
Branched GAP	2088.1 (26.8)	N/D	-
HTPB R45HT	1310 (42.8)	1232 (45.6)	1202 (46.7) [21][c]

[a] Functionality values are in the brackets and are in mg KOH/g.

[b] Method used to deterime OHV not known.

[c] Determined via acetic anhydride/pyridine titrimetric method.

Further end-group analysis includes the measurement of residual monomer and oligomer percentages (oligomers are short chain polymers, 2-10 monomer units long). Such data is sought to gauge how much oligomer to polymer is present and purity levels. This information can be readily obtained via NMR spectroscopy during analysis for OH Values (refer Appendix C).

NMR spectroscopy results indicate that the as-received polyGLYN is of a significantly purer nature than either of the polyNIMMO polymers, with oligomer percentages in the 3-4% range, whereas polyNIMMO polymers both gave values around 11-12.6%. For polyNIMMO, this accounts for a product that has approximately 88-89% polymer with the remainder oligomer and a small amount of monomer, *c.f.* polyGLYN which is approximately 96% polymer. This may be due to chemical degradation of the polymer chains and end groups, incomplete polymerisation during production, or possibly monomer polymerisation if there is any active catalyst present. The following data has been calculated thus:

Polymer	Monomer, %	Oligomer, %
PolyNIMMO PP670	0.29	12.6
PolyNIMMO PP650	0.32	11.0
PolyGLYN	0.15	3.4

4.2 Polymer Sensitivity Testing

Small-scale hazard assessment data for the polymers are given in Table 7. Note that some polymers are not classified as explosive, polyGLYN and polyNIMMO are classed as non-explosive while GAP has a hazards rating of 1.3. Impact and electrostatic discharge were not measured as the required equipment was for testing of liquids (values quoted are from literature sources). Temperature of ignition and friction tests compared well with manufacturer specifications (reference values are given in brackets).

Table 7: Small-scale Hazard Assessment

Polymer	T of I, °C	F of I	ESD, J	F of F, N	Ref.
GAP	220 (247)	187.5	No ignition at 4.5 J	>360	[34]
B-GAP	250 (252)	140	No ignition at 4.5 J	>360	[21]
PolyNIMMO PP670	163 (165)	140	No ignition at 4.5 J	>360	[21], [35]
PolyNIMMO PP650	168 (165)	140	No ignition at 4.5 J	>360	[21]
PolyGLYN	170 (170)	140	No ignition at 4.5 J	>360	[23]

4.3 Binder Systems Characterisation

Most binder systems were cured with a 50:50 N100/IPDI mixture at a ratio of 1.1:1 isocyanate/polymer hydroxyl. However the manufacturers recommendation of 100% N100 was adopted for the satisfactory cure of polyNIMMO. Formulation numbers are given from **38** to **43E**, with the E designating an energetic binder system. Once binders were cured, hardness measurements were recorded after three days, followed by thermal analysis and vacuum stability tests in order to gauge any compatibility issues.

4.3.1 Mechanical Properties - Hardness Measurements

The main objective of hardness measurements is to establish the minimum time required to obtain an acceptable level of cure and to establish the effect of filler sedimentation and any migration of binder/plasticisers. Hardness measurements were performed on cured rubbers three days after removing from vacuum oven (Table 8).

Table 8: Shore Hardness of Rubbers (38 to 43E)

Formulation Number	Binder Contents	Hardness* (±2.0)
38	HTPB/IPDI/N100	56.3
39E	PolyNIMMO 670/N100	48.3
40E	PolyNIMMO 650/N100	42.0
41E	PolyGLYN/IPDI/N100	36.7
42E	GAP XL/IPDI/N100	30.2
43E	B-GAP/IPDI/N100	40.2

*Average value taken over 5 measurements

Hardness in the more mechanically sound HTPB formulation is greater than in the energetic binder formulations. The GAP formulations reveal the lowest hardness values, followed by polyGLYN and polyNIMMO.

4.4 Compatibility Tests of Binder System

4.4.1 Vacuum Stability Tests of Binder System

Vacuum stability tests were carried out at 100°C for 40 hr (Table 9) as testing of these materials at higher temperatures (120°C) results in excessive gassing. The acceptance criteria 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" [36]. All rubber formulations showed good stability when fully cured. Trifunctional polyNIMMO exhibits the highest gassing rate of 1.27 mL/g.

Table 9: Vacuum Stability Tests at 100°C

Formulation	Evolved Gas, mL/g
38	0.14
39E	0.89
40E	1.27
41E	0.93
42E	0.86
43E	0.58

4.4.2 Thermal Stability Analysis

Thermal stability studies on the cured binder rubbers have also been conducted (Table 10). All binders possess low glass transition temperatures with high decomposition points, implying good thermal stability suitable for use in munitions.

Table 10: Thermal Properties of Rubbers (38 - 43E)

Formulation Number	Binder Contents	DSC		TGA
		Tg, °C	Decomp., °C	Weight loss, %
38	HTPB/IPDI/N100	-88	>465	8.1% at 305°C 8.7% at 390°C 7.6% at 440°C
39E	PolyNIMMO PP670/N100	-25	185	11.1% at 220°C
40E	PolyNIMMO PP650/N100	-14.5	193	41.7% at 240°C
41E	PolyGLYN/IPDI/N100	-23.4	195	17.4% at 235°C
42E	GAP XL/IPDI/N100	-39.4	220	82.5% at 230°C
43E	B-GAP/IPDI/N100	-28.8	>235	41.6% at 220°C

It is further apparent from these results that very good thermal characteristics are exhibited by the hydroxy-terminated polybutadiene (Tg of -88°C and decomposition point of > 465°C). While the energetic binder systems possess extra available energy for detonation, they suffer as a result of their poorer thermal properties over the inert HTPB. Nevertheless, the energetic binders possess workable low glass transition points and relatively high decomposition temperatures making their use in munitions attractive.

If one is to consider the current UK operational requirement for the air carriage of munitions (ranges from -55°C to 71°C [37]), then all of these binders show good thermal stability and have no problem reaching the upper operational limit. However, it is at the lower operational limit of -55°C that most energetic binders fail to perform, it is here where free chain mobility becomes hindered below the polymer's glass transition temperature. This may necessitate the use of better processing aids to plasticise energetic binders for air carriage ordnance.

On the other hand, use of energetic binders in land or sea environments requires a higher Tg than for airborne ordnance systems since munitions requirements are less severe than for these environments . Consideration should also be given to the fact that the binder glass transition temperature increases with higher formulation solids loading and applied strain rate and thus thermal analysis needs to be performed on all systems, both filled and unfilled.

4.4.3 Temperature of Ignition Determination

Small-scale hazard assessment data for the binders are given in Table 11. Only T of I has been measured; friction, impact and electrostatic discharge were not determined as the required equipment was unavailable.

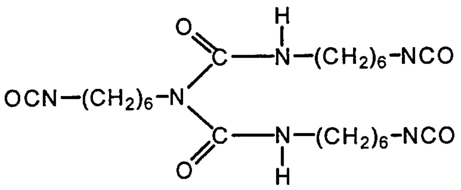
Table 11: Small-scale Hazard Assessment

Formulation Number	Binder	T of I, °C
38	HTPB	400
39E	PolyNIMMO (di-func.)	177
40E	PolyNIMMO (tri-func.)	174
41E	PolyGLYN	163
42E	XL-GAP	205
43E	B-GAP	221

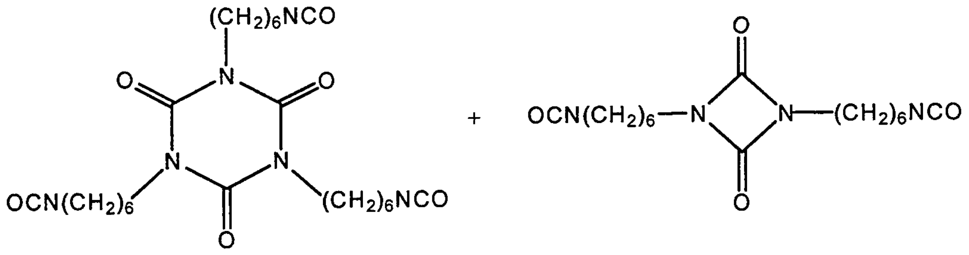
5. Comparison of Alternative Isocyanate Curing Agent Desmodur N3400 versus Desmodur N100

Desmodur N100 is commonly used for curing polyNIMMO and polyGLYN, but leads to the formation of brittle polymers [14]. In common with HTPB and GAP, polyGLYN is typically cured with a 50:50 mixture of N100 and isophorone diisocyanate, (IPDI) to afford an adequate cure. It has been observed that the mechanical properties of cured polyGLYN rubbers are inferior to those of inert HTPB [14]. The polyGLYN rubbers are soft and break easily while HTPB rubbers are firm and have relative strength.

N100



N3400



Isocyanate Trimer **Uretidone Dimer**

It was recently reported that a 75:25 N100/IPDI mixture had superior cure properties over the 50:50 mixture routinely used for polyGLYN at DERA, although the rubbers still lack the required mechanical strength of inert HTPB formulations [14]. It was strongly recommended that alternative cross-linking isocyanates should be trialed at similar ratios. Experiments were therefore conducted with IPDI and varying ratios of N100 and the alternative Desmodur N3400 (Desmodur N3400 is a low viscosity, solvent free aliphatic polyisocyanate based on hexamethylene diisocyanate and comprises an isocyanurate trimer and uretidone dimer. N100 is also derived from hexamethylene diisocyanate). A series of polyGLYN formulations was prepared, cured with IPDI and mixed with either N100 or N3400 at various ratios (25, 50, 75 & 100%) according to Table 12. These rubbers were screened for mechanical properties, namely, hardness and tensile strength.

Table 12: Formulation and Hardness Data. All formulations contain 5 ppm dibutyltin dilaurate as catalyst.

Formulation	Ingredients	Wt, %	Appearance	Hardness*
44E	PolyGLYN Desmodur N3400	82.0 18.0	Clear yellow	41.0
45E	PolyGLYN Desmodur N100	82.0 18.0	Clear yellow	53.0
46E	PolyGLYN Desmodur N3400 IPDI	83.5 13.6 5.65	Clear yellow	30.3
47E	PolyGLYN Desmodur N3400 IPDI	85.2 9.1 5.7	Clear yellow	21.5
48E	PolyGLYN Desmodur N3400 IPDI	87.0 4.5 8.5	Clear yellow	14.2
50E	PolyGLYN Desmodur N100 IPDI	83.7 13.5 2.8	Clear yellow	34.2
51E	PolyGLYN Desmodur N100 IPDI	85.3 9.0 5.7	Clear yellow	28.3
52E	PolyGLYN Desmodur N100 IPDI	87.0 4.5 8.5	Clear yellow	15.3

*Average value taken over 5 measurements.

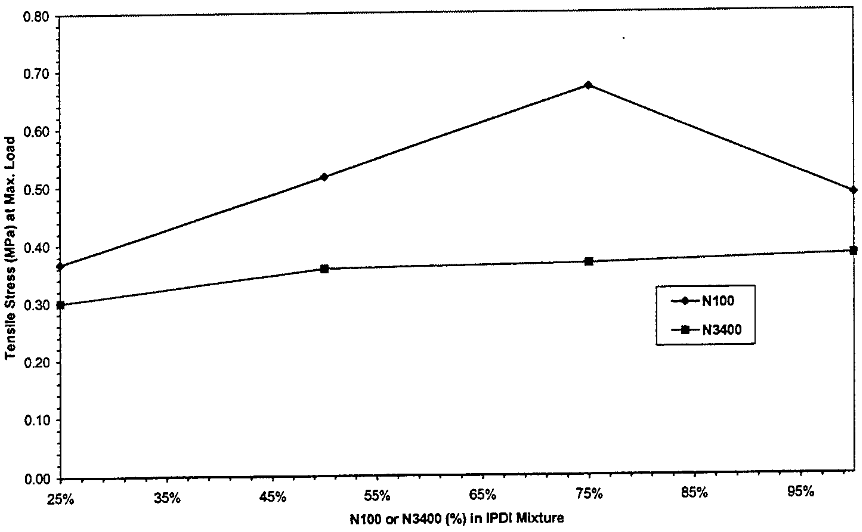


Figure 4: Analysis of Tensile Strength of PolyGLYN versus Percentage of N100 or N3400 in an IPDI/(N100 or N3400) Mixture.

Results for the tensile strength tests and maximum load versus percentage of N100 or N3400 in an IPDI/(N100 or N3400) rubber are displayed in Figures 4 and 5 and indicate that the 75% N100 mixture forms the best rubber by this test. This is further confirmation of prior research conducted at DERA [14].

N3400 crosslinker agent does not appear to confer any additional benefit over N100. It should be stressed that these are unfilled rubber systems and not filled with organic materials like RDX, HMX, etc. Incorporation of such fillers into the rubbers would require further testing to evaluate filled systems.

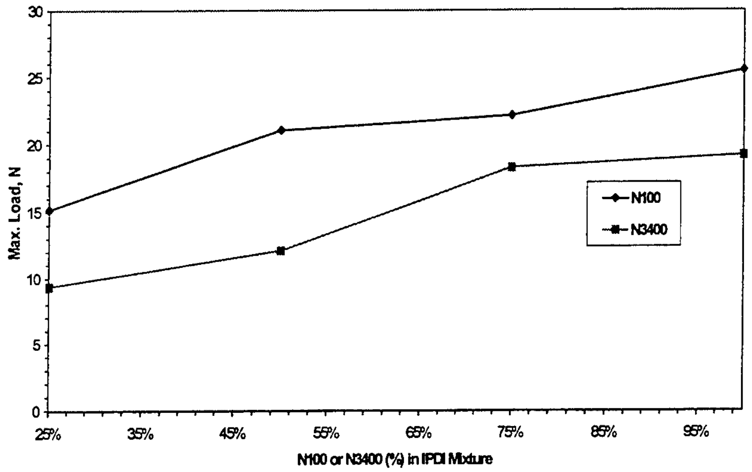


Figure 5: Analysis of Maximum Load Strength of PolyGLYN versus Percentage of N100 or N3400 in an IPDI/(N100 or N3400) Mixture.

6. Conclusions and Recommendations

Current PBX service munitions comprise binders based primarily on hydroxyl-terminated polybutadienes, which confer good mechanical properties to the explosive but offer no additional energy to the system. Energetic binders, such as polyNIMMO, polyGLYN and GAP offer energy increases to the PBX but exhibit inferior mechanical properties to HTPB. The next generation of munitions is likely to incorporate these polymers leading to a new wave of high performance IM compliant munitions.

Both polyGLYN and polyNIMMO are expensive materials and are currently better suited for fills in high cost, high performance munitions that inevitably have space restrictions with respect to warhead size. Eventually, the currently prohibitive cost of energetic binders may become more affordable and thus more likely to be used in conventionally filled munitions. In addition, the use of energetic plasticisers to further modify mechanical properties of the binder systems is vital.

In an effort to improve the mechanical properties of the binder systems discussed herein, an alternative cross-linking agent (Desmodur N3400) was assessed and compared to Desmodur N100. Our results indicate that N100 cross-linking still remains the superior cross-linker over the N3400.

This report serves to fully characterise polymers and evaluate binder properties for use in military ordnance by the ADF. Three major energetic polymers have been readily characterised and polymerisation studies undertaken to effectively gauge polymerisation conditions. It is anticipated that such systems will be utilised in IM-compliant high perfromance explosives and propellants in the near future.

7. References

1. Australian Defence Organisation, (1993), *Insensitive Munitions*, Defence Instruction (General) DI(G) LOG 07-10, Canberra.

2. Peters, G.S., Gorham, S.D., Smith, F.J., Fraser, A.M., Colclough, M.E., Millar, R., (2000), Ozone Degradation Study of Novel Chain Extended Energetic Polymers Containing Carbon-Carbon Double Bonds, *Prop. Expl. Pyro.* **25**, 191-198.

3. Nissan, R.A. and Cramer, R.J., (1986), Equivalent Weight and Functionality Determinations of Polyols by Trifluoroacetylation and ^{19}F NMR Analysis, *JANNAF Propulsion Characterization Subcommittee Meeting*, Monterey, CA, 18-21st November.

4. Nissan, R.A., Quintana, R.L., Manser, G.E., Fletcher, R.W., (1987), Analysis of Oxetane Thermoplastic Elastomers. NMR Methods, *JANNAF Propulsion Meeting*, San Diego, CA, 15-17th December, JANNAF.

5. Wardle, R.B., Cannizzo, L.F., Hamilton, R.S., Hinshaw, J.C., (1992), *Energetic Oxetane Thermoplastic Elastomer Binders*, Contract Number N00014-90-C-0264, Thiokol Corp., Brigham, UT.

6. Oberth, A.E., (1978), Functionality Determination of Hydroxyl-Terminated Polymers, *AIAA* , **16**, (9), 919.

7. Groom, T., Babiec, J.S., Jr., VanLeuwen, B.G., (1974), End Group Analysis of Polyether Polyols by Nuclear Magnetic Resonance (NMR) Spectroscopy, *J. Cell. Plast*, **10**, (1), 43-5.

8. Grant, D.M. and Paul, E.G., (1964), Carbon-13 Magnetic Resonance. II. Chemical Shift Data for the Alkanes, *J. Am. Chem. Soc.*, **86**, 2984-90.

9. Lindeman, L.P. and Adams, J.Q., (1971), Carbon-13 Nuclear Magnetic Resonance Spectrometry. Chemical Shifts for the Paraffins Through C_9, *Anal. Chem*, **43**, 1245.

10. DeThomas, F.A., Hall, J.W., Monfre, S.L., (1994), Real-Time Monitoring of Polyurethane Production Using Near-Infrared Spectroscopy, *Talanta*, **41**, (3), 425-431.

11. Billmeyer, F.W., Jr., (1971), *Textbook of Polymer Science*, John Wiley & Sons, New York, pp 52-56.

12. Cramer, R.J., (1987), *Molecular Weight Determination of Energetic Polymers By Low Angle Laser Light Scattering*, NWCTP6774, NWC, CA.

13. Whitehead, P.M., *Propellant Testing* - Metrology, OSD Propulsion Data Sheet PDS245, DSTO.

14. Cliff, M., (1999), *PolyGLYN Binder Studies and PBX Formulation: Technical Achievements from a LTA to DERA Fort Halstead,* DSTO-TR-0884, DSTO, Salisbury, SA.

15. UK Sensitiveness Collaboration Committee, (1988), *Explosives Hazard Assessment, Manual of Tests,* SCC No. 4, (a) Test No. 1/88, (b) Test No. 3/88.

16. Australian Defence Standard, (1980), *Methods of Test for Explosives and Related Materials,* Method 3/80.

17. (1975), American National Standard ASTM-D2240, *Indentation Hardness of Rubber and Plastics by Means of a Durometer,* 702-704.

18. Desai, H.J., Cunliffe, A.V., Millar, R.W., Paul, N.C., Stewart, M.J., Amass, A.J., (1996), Synthesis of narrow molecular weight α,ω-hydroxy telechelic poly(glycidyl nitrate) and estimation of theoretical heat of explosion, *Polymer,* **37**, (15), 3471-3476.

19. Meßmer, A. and Böhnlein-Mauß, J., (1997), Untersuchungen zum Einsatz von POLYNIMMO in Treibladungspulvern, *28th Int. Ann. Conf. ICT,* Karlsruhe, Federal Republic of Germany, 24th-27th June, Fraunhofer-Institut für Chemische Technologie, 116-1.

20. Willer, R.L. and Day, R.S., (1989), Poly(Glycidyl Nitrate) Revisited, *ADPA Int. Symp. Comp. of Plastics and other Materials with Explosives, Propellants, and Pyrotechnics and Processing Propellants, Explosives and Ingredients,* Virginia Beach, VA, 23-25 Oct., APDA(s): APDA.

21. (1996), *Characterization of New Propellant Ingredients,* KTA-17 Final Report, TTCP.

22. Shephard, R., (1995), *Measurement of the Microstructure of Hydroxy Terminated Polybutadiene,* DRA/WSS/WX4/DWI/042/1, DRA, Weapons Systems Sector.

23. ICI Explosives, (1998), ICI Explosives Product Information, SAAPS015.

24. Bocksteiner, G. and Billon, H., (1992), *Insensitive Polymer Bonded Main Charge Explosive PBXW-115: Binder and Formulation Studies,* MRL-TR-91-54, AMRL, DSTO.

25. Colclough, M.E., Desai, H., Millar, R.W., Paul, N.C., Stewart, M.J., Golding, P., (1993), Energetic Polymers as Binders in Composite Propellants and Explosives, *Polymer,* **5**, 554-560.

26. Boiki, V.P. and Grishchenko, V.K., (1985), Determination of Hydroxyl Groups in Polymers, *Acta Polymirica Acta,* **36**, 459-472.

27. Kim, C.S.Y., Dodge, A.L., Lau, S.F., Kawasaki, A., (1982), Determination of Hydroxyl Concentration in Polymers from the IR Adsorption Band of THF Associated OH Groups, *Anal. Chem.,* **54**, 232.

28. Druet, L. and Boucher, Y., (1988), *Application of ^{1}H NMR Spectroscopy to Hydroxyl Group Determination in Propellants and Explosives,* R-4499/88, DREV, Canada.

29. Cannizzo, L.F., Hajik, R.M., Highsmith, T.K., Sanderson, A.J., Martins, L.J., Wardle, R.B., (2000), A New Lost-cost Synthesis of PGN, *31st Int. Ann. Conf. ICT*, Karlsruhe, Federal Republic of Germany, 27th-30th June, Fraunhofer-Institut für Chemische Technologie, 36-1.

30. 3M Specialty Chemicals Division, (1991), *Hydroxyl Equivalent Weight of GAP (N-methylimidazole Method)*, QCM#76.17, 3M Specialty Chemicals Division.

31. Shephard, R., (1995), *Quantitative Determination of the Hydroxyl End Group, Residual Monomer and Oligomer Content for Poly (3-Nitratomethyl-3-methyloxetane), (PolyNIMMO) Using* ^{13}*C NMR Spectroscopy.*, DRA/WSS/WX4/DWI/038/1, DRA.

32. Shephard, R., (1995), *Work Instruction for Quantitative Determination of Hydroxyl Content for PolyGLYN Using* ^{13}*C NMR Spectroscopy*, DRA/WSS/WX4/DWI/037/1, DRA.

33. Shephard, R., (1995), *Measurement of the Hydroxyl Content of Hydroxyl Terminated Polybutadiene*, DRA/WSS/WX4/DWI/043/1, DRA.

34. Graham, K.J., Williams, E.M., Lynch, R.D., Floyd, T.G., Struck, S.R., (1994), Reducing the Sensitivity of High-Performance Warhead Fills, *Insensitive Munitions Technology Symposium*, VA, 21-24th March, American Defense Preparedness Association, 541-563.

35. ICI Explosives, (1995), ICI Explosives Product Safety Data Sheet.

36. Lamy, P., Leiber, C-O, Cumming, A.S., Zimmer, M., (1996), Studies of High Energy Insensitive High Explosives, *27th Int. Ann. Conf. ICT*, Karlsruhe, Federal Republic of Germany, Fraunhofer-Institut für Chemische Technologie, 1-1.

37. Maxey, I.H., (1996), Environmental Data for Rocket Motor Service Life Assessments, *AGARD Conference 586 - Service Life of Solid Propellant Systems*, Athens, Greece, 10-14 May, AGARD, 39(1).

38. Manzara, A.P., Johannessen, B., Denenholz, I.M., (1994), Characterisation of GAP Polyol and Plasticizer, *25th Int. Ann. Conf. ICT*, Karlsruhe, Germany, 25-28th June, Fraunhofer-Institut für Chemische Technologie, 73-1.

39. Cliff, M. (2001), personal communication.

Appendix A: Titrametric Method for the Determination of Hydroxyl Equivalent Weight Numbers

The procedure describe here is based on [38]. The technique involves the *N*-methylimidazole base catalysed acetylation of polymers containing terminated hydroxyl groups and gives a reliable estimate of hydroxyl equivalent weight numbers. Such numbers are then used to accurately determine the amount of isocyanate needed to form a favourable elastomeric network with the polymer.

Titrametric Method

The following solutions were made up:

1. Acetic anhydride: Pipette 15 mL acetic anhydride to a 100 mL volumetric flask, dilute to the mark with 1,2-dichloroethane. Mix thoroughly and transfer contents to a brown bottle.
2. Methanolic 0.5 N potassium hydroxide: A standardised 'VOLUCON' potassium hydroxide (N/10) is poured into a 200 mL volumetric flask and topped up with methanol. Shake and leave to stand.
3. Methanol (15%) in chloroform. Add 150 mL methanol to 850 mL chloroform in a volumetric flask.
4. Phenolphthalein (1%): Dissolve 1.0 g phenolphthalein into 100 mL methanol .
5. Polymer in 1,2-dichloroethane: 5.00 g of polymer is placed into a 500 mL conical flask. 20 mL 1,2-dichloroethane is then placed into the flask and allowed to stand overnight. Shake well at repeated intervals.

Procedure:

A thermocirculating water bath was run at 60.0±2.0°C for several days prior to analysis. Polymer analysis was carried out in duplicate.

1. A blank was prepared by placing 20 mL 1,2-dichloroethane into a 500 mL conical flask.
2. Stir polymer samples and add 4 mL of the acetic anhydride solution to each sample.
3. While stirring, add 4 mL *N*-methylimidazole to samples. Stir for 1 min.
4. Place flasks into 60°C water bath for 30 mins.

5. Remove flasks from bath and add 3 mL deionized water to each flask. Stir for 1 min.
6. Place flasks back into water bath for an additional 10 mins.
7. Remove flasks and allow to cool.
8. Add 250 mL of 15% v/v methanol in chloroform solution to each flask and stir.
9. Add phenolphthalein (3-4 drops).
10. Titrate solutions with 0.5 N methanolic potassium hydroxide solution and record titre values at the end-point.

Equivalent weight numbers and functionality are determined from the following:

$$\text{OH Eq. Wt.} = \frac{(\text{wt. of polymer}) * 1000}{(V_{\text{blank}} - V_{\text{sample}}) * \text{N}} \qquad \text{(A1)}$$

Where N is the normality of the potassium hydroxide solution.

$$\text{Functionality} = \frac{56100}{\text{OH Eq. Wt.}} \qquad \text{(A2)}$$

Appendix B: NMR Spectroscopic Method for the Determination of Hydroxyl Equivalent Weight Numbers

The procedure describe here is based on [31, 32] and involves the use of carbon^{13} NMR spectroscopy, with a suitable relaxation agent such as chromium acetylacetonate, to accurately measure equivalent weight numbers for hydroxy-terminated polymers.

Procedure:

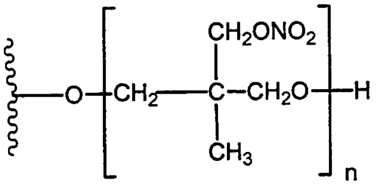
1. Preheat polymer to 60°C.
2. Weigh 2.0 g into a 5 mm NMR sample tube
3. Add 0.07 g chromium acetylacetonate and then 4.0 g $CDCl_3$ (for polyNIMMO) or d_6-acetone (for polyGLYN).
4. Shake tube well, sample is now ready for NMR analysis.
5. Run NMR spectral analysis under following conditions: NT = 20 000, decoupling mode = Inverse gated decoupling, SW = 20 000 Hz, D1 = 3 to 5 ms and LB = 3.0 (line broadening).
6. Collect scans and process as for normal NMR analysis.
7. Final analysis requires different peak area measurements for both polyNIMMO and polyGLYN.

PolyNIMMO Hydroxyl Calculations

To calculate hydroxyl content it is necessary to measure the area of a peak due to the methyl carbon of the polymer backbone and the areas of the peaks due to the hydroxyl end group carbons. These peaks are measured as individual peaks and the areas summed in calculation. Peaks are integrated via the spectrometer integration routine and are in shown in the representative spectrum (Figure B-1).
Hydroxyl content for Poly NIMMO can therefore be given by:

$$OH = \frac{1000(E' + E + C)}{147A} \text{milliequivs/g} \qquad \text{(A3)}$$

Where 147 is the repeat unit weight of the repeat unit:



$$-O-\left[CH_2-\overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_3}{C}}-CH_2O\right]_n-H$$

A is the integral under the methyl peak, while *E′* and *E* are discussed below. *C* is not part of the polyNIMMO molecule, rather it is based on the hydroxy-terminated carbon of butane-1,4-diol, an initiator from the synthesis of polyNIMMO.

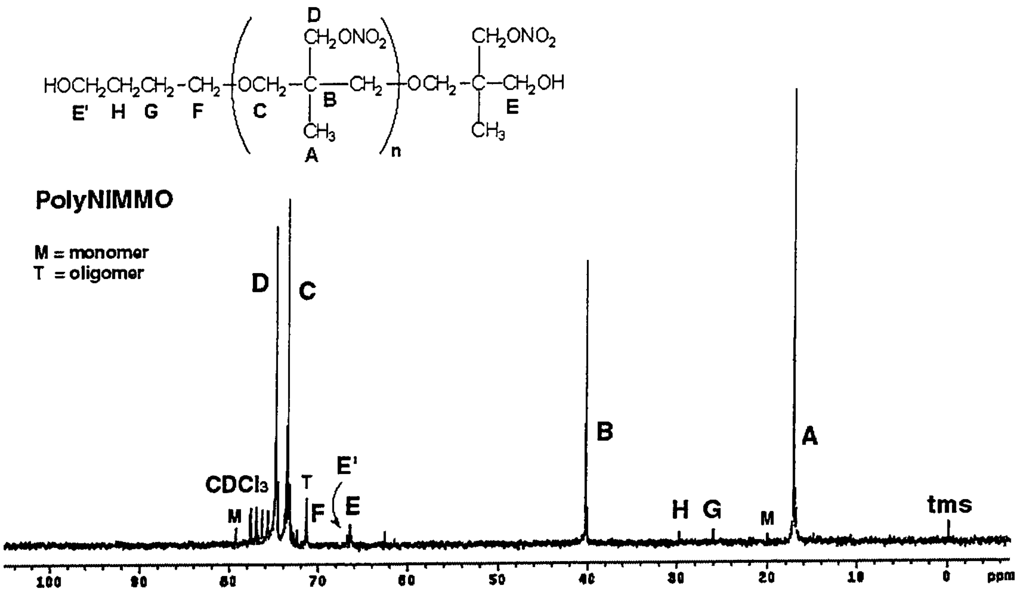


Figure B-1: ^{13}C NMR Spectrum of PolyNIMMO

The monomer resonances are marked in the spectrum above (M), as are oligomer units (T), the oligomer peak shown at 71 ppm belongs to the shoulder peak, the main peak is F (see Figure B-1). Note that the large peak at 40 ppm belongs to the quaternary carbon of the polyNIMMO unit while resonance **C** (not to be confused with **C** of equation A3) belongs to the methylene ether linkages. Resonance **G** belongs to the methylene carbon of the initiator fragment, while **E** is due to the CH_2OH groups of the polymer chains and **E′** (found directly adjacent to **E** at 67.0 ppm) is due to the ethoxy end group.

One of the most important differences between polyNIMMO and polyGLYN is positioning of the butane diol fragment in the polymer chain. For polyNIMMO, the butane diol fragment occurs at the end of the polymer chain while for polyGLYN, it is found in the centre of the polyGLYN polymer. This has been verified by reacting both polymers with trifluoroacetyl anhydride and observing whether any discernible differences occur at the butane diol resonances (29.5 and 26.0 ppm) in the ^{13}C NMR [39]. For polyGLYN, no differences are observed whereas for polyNIMMO, shifts due to the anhydride groups are observed.

In an effort to clearly define all resonances in the NMR spectra for both polyNIMMO and polyGLYN, 2D NMR was necessary to accurately assign each resonance to a specific group. A COSY 2D NMR experiment was performed to elucidate nearest neighbour coupling and to clearly define proton resonances. Starting from the unambiguously assigned resonance of **A** at 0.8 ppm and drawing the cross peaks immediately indicates further resonances. In this case, resonance **B** occurs at 3.1 ppm while resonance **C** occurs at 4.1 ppm. To show correlation between heteronuclear species (i.e. proton and carbon) a HETCOR 2D NMR was also performed (Figure B-2). For HETCOR NMR, the x-axis corresponds to the ^{13}C NMR spectrum with the y-axis corresponding to the ^{1}H NMR spectrum. It can be clearly seen that the methyl carbon of the polyNIMMO backbone repeating unit occurs at 17 ppm in the carbon NMR and 0.8 ppm in the proton NMR. Assignment of resonances is thus: methylene nitroso carbon is found at 75 ppm (4.5 ppm in the proton NMR) with the methylene ether group occurring at 73 ppm (3.1 ppm in the proton NMR). Note that the quaternary carbon does not appear in the spectrum below as it shows no coupling to protons (both the ^{1}H and ^{13}C spectra on the HETCOR plot are projections based on the software, and not actual NMR spectra). This accounts for the absence of peak B in Figure B-2.

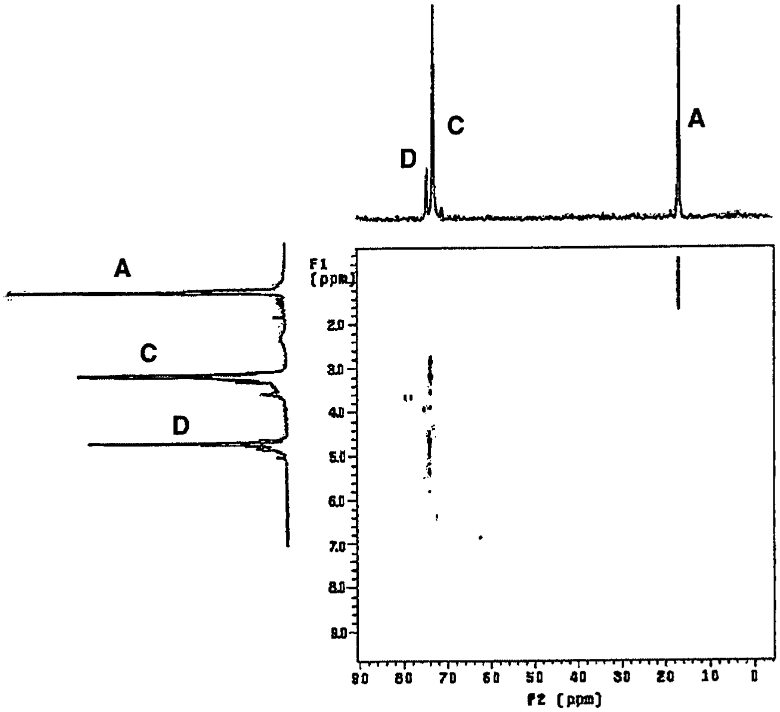


Figure B-2: 2D NMR – HETCOR Spectrum of PolyNIMMO

PolyGLYN Hydroxyl Calculations

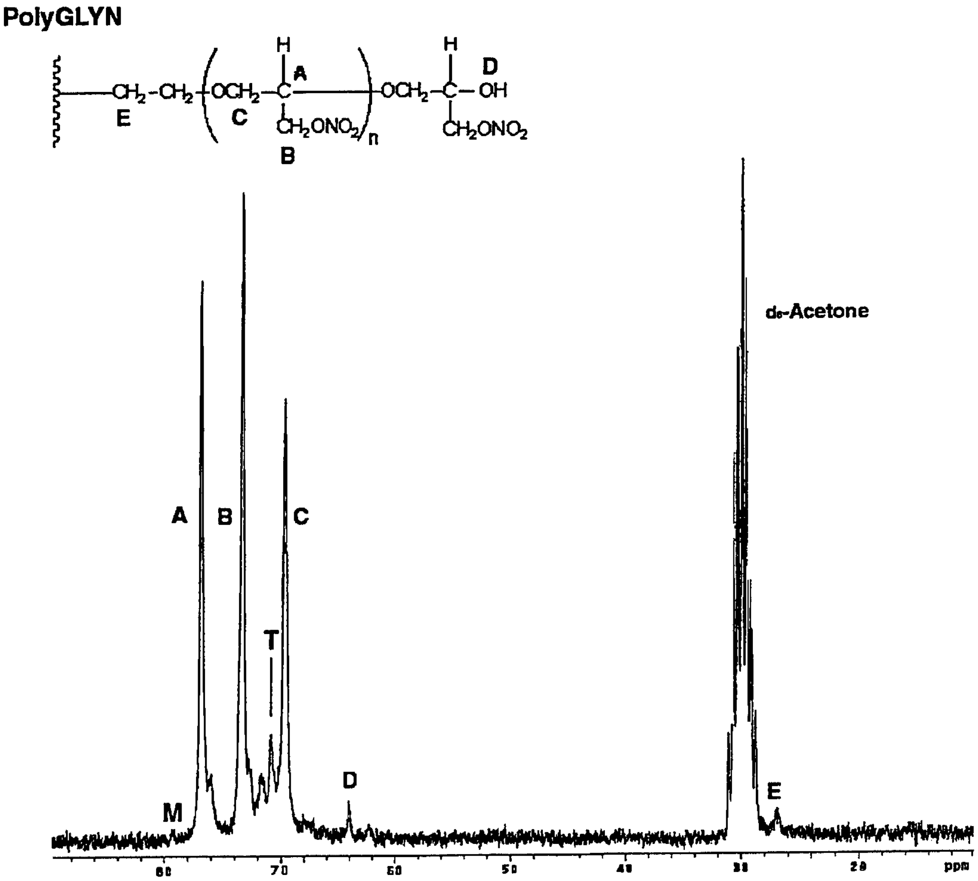
For polyGLYN, the hydroxyl number is calculated via the following formula [32]. Peak assignments are given in the representative spectrum (Figure B-3). Also, the various numbers associated with each specific resonance are simply the atomic weights of each particular functional group. **D** is the methylene carbon directly attached to the hydroxyl end group (64 ppm) with **E** the methylene carbon of the butanediol initiator (27 ppm):

$$OH = \frac{\boldsymbol{D}*1000}{(120.09*\boldsymbol{D}+119.08*\boldsymbol{A}+22.03*\boldsymbol{E})}\text{milliequivs/g} \qquad (A4)$$

The NMR spectra of polyGLYN are compounded by the fact there is a chiral centre leading to tacity effects and head to tail, tail to tail and head to head effects. For comparative purposes, the spectra of polyGLYN closely resembles polyepichlorohydrin (precursor to glycidyl azide polymer, GAP) and is given in Figure B-4.

Due to the complicated and broad NMR spectra, 2D NMR techniques - COSY and HETCOR have been performed as for polyNIMMO. Analysis confirms the C-H peak (**A**, 77 ppm), the methylene nitroso unit at 73 ppm (**B**) and the OCH_2 (**C**) functionalities at 69 ppm. The C-H assignment is based on a similar C-H assignment of polyECH (C-H assigned at 79.6 ppm) [39]. In addition, the backbone OCH_2 should have similar shifts as for the ECH (see Figure B-4). ECH has a shift of 70 ppm for the OCH_2 functionalities, in polyGLYN however, there are present two large resonances belonging to the OCH_2 and the methylene nitroso groups.

Figure B-3: ^{13}C NMR Spectrum of PolyGLYN (Monomer = M and oligomer = T)



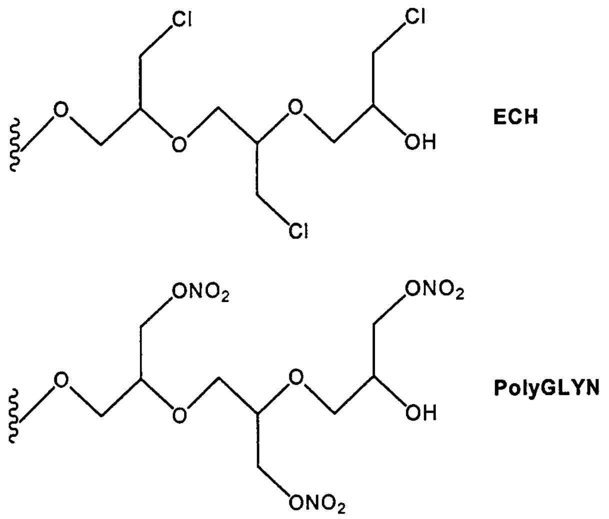


Figure B-4: Polyepichlorohydrin (ECH) and PolyGLYN Similarities

Appendix C: NMR Spectroscopic Method for the Determination of Residual Monomer and Oligomer Content

The determination of end-groups by NMR spectroscopy also permits the measurement of residual monomer and oligomer percentages. Residual monomer is simply whether any monomer is left residing in the rubber after polymerisation and work-up procedures have taken place. Oligomers or short chain polymers, are typically comprised of between 2-10 monomer units for both polyNIMMO and polyGLYN rubbers. Oligomers are a consequence of the polymerisation conditions and therefore unavoidable, but preferably kept low, hence the need for accurate determination of monomer and oligomer contents.

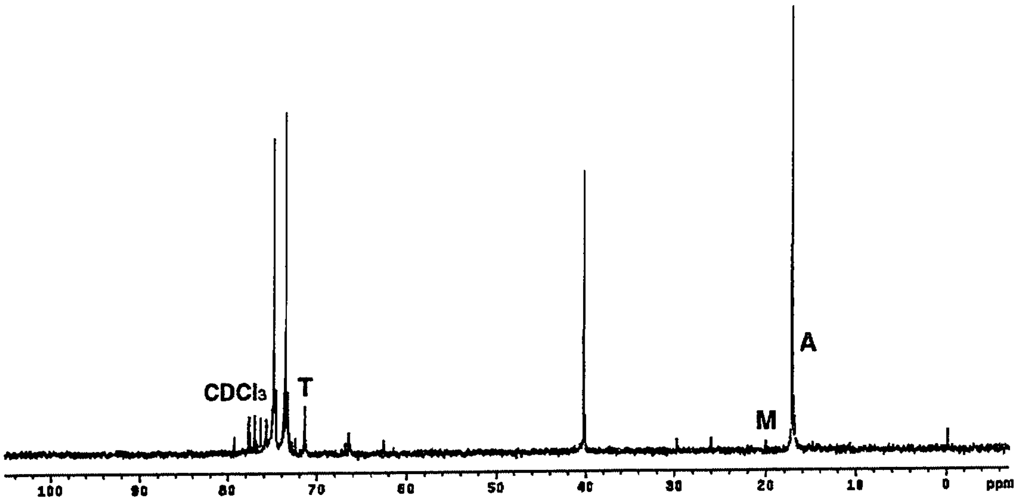
The analysis of monomer and oligomer content involves the following formulae [31]:

$$\text{Residual Monomer: } \left(\frac{M}{A+M}\right)*100\ \%\ \text{w/w} \qquad \text{(A5)}$$

$$\text{Oligomer Content: } \left(\frac{1/2T}{A+1/2T}\right)*100\%\ \text{w/w} \qquad \text{(A6)}$$

where A = CH_3 resonance for polyNIMMO and C-H resonance for polyGLYN, M = monomer resonance and T = oligomeric OCH_2 resonance present in both polyGLYN and polyNIMMO (T is the shoulder peak at 71.5 ppm in Figure C-1). For polyGLYN, M is found at 79.0 ppm while T occurs at 71.0 ppm (spectrum not shown).

Figure C-1: ^{13}C NMR Spectrum of PolyNIMMO (integration not shown).



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19. ABSTRACT

In order to comply with Insensititive Munitions (IM) criteria, energetic binders comprising polymer and plasticiser(s) are finding use in cast-cured polymer bonded explosives and cast composite rocket propellants. Energetic binder systems confer energy output increases over conventional inert binder systems currently in use, and are thus of interest to the ADF. This report serves to characterise fully the physico-chemical properties of such energetic binder systems.

Both the uncured 'prepolymer' binder and the fully cured system have been characterised by various techniques including thermal analysis, spectroscopic analysis, sensitivity tests, molecular weight chromatography and mechanical properties. Detailed cure information obtained from these analyses are used to ensure effective cure.