

## Review of Polyglycidyl Nitrate – An Energetic and Promising Polymer as a Binder Propellant

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### Abstract

The propellant binder is one of the important components in three-component-based propellants. Three-component-based propellants contain oxidizer, binders, and additives. Refers to specific impulse value and combustion rate, polyglycidyl nitrate is a very promising energetic polymer as a propellant binder. Polyglycidyl nitrate has the potential to be made from glycerol which is a waste of the biodiesel industry so that production costs are cheaper. This article discusses in depth the potential of polyglycidyl nitrate as a propellant energetic binder, including the composition of the propellant, the effect of the propellant binder on the properties of the propellant, the manufacture of polyglycidyl nitrate from glycerol, as well as the physical properties and thermodynamic data of Polyglycidyl nitrate.

*Keywords:* binder, energetic material, polyglycidyl nitrate, propellant

### 1. Introduction

The propellant is the fuel in a rocket and can be used in guns [1]. The heat generated from the combustion of the propellant constituent materials is used as propulsion for the rocket. Materials classified as propellants include black powder, smokeless powder, rocket propellants, and liquid propellants [2]. Another categorization states that there are 2 propellants, namely liquid propellant, and solid propellant. The first propellant used for rockets was liquid propellant. Solid propellants have the following advantages: simplicity, energy storage capability, high thrust, and flow during launching [3]. Thakre and Yang [4] determined that solid propellants consist of two types, homogeneous propellants, and heterogeneous (composite) propellants. Pradhan et al. [5] stated that solid propellant has 2 basic components, i.e. fuel, and oxidizing agent.

Homogeneous propellants are divided into three categories: single base propellant, double base propellant, and triple base propellant. Single base propellants are propellants that are composed of only one type of component and have both reducing and oxidizing properties simultaneously. This compound is usually nitrocellulose. A two-component base propellant is a colloidal form of a mixture of nitroglycerin and nitrocellulose. Triple base propellants contain binders, oxidizing agents, and additives [6]. Additive materials include plasticizers, curing agents, stabilizers, and cross-linking agents [7]. Provatas [8] stated that the propellants developed were three-component base propellants because of their ease of handling, better ballistic and energetic properties. The combination of an energetic binder and an energetic oxidizer will increase the specific impulse up to 300 times and reduce pollution [9].

Binder propellant is a material that reacts with a curing agent to obtain a mesh-shaped composite molecular structure and functions as fuel and has active groups at both ends.

Binder affects the physical and mechanical properties of the propellant, the process of making the propellant, and the life of the propellant [7]. There are two kinds of propellant binders, i.e non-energetic polymers, and energetic polymers. At the beginning of development, the binders used were usually non-energetic polymers such as poly caprolactam, polyethylene glycol, and polybutadiene. Since around 1950, energetic binders have been developed with satisfactory mechanical properties and have a higher energy level or specific impulse (Isp) in a propellant formulation. In recent developments, an energetic polymer is preferred to replace HTPB because it has a specific impulse and higher combustion rate. The use of energetic polymers also increases the density and combustion temperature [9]. This study discusses the potential of polyglycidyl nitrate as an energetic binder propellant. The discussion starts from the composition of the propellant, the effect of the propellant binder on the properties of the propellant, then describes in detail the manufacture of polyglycidyl nitrate along with the techniques for PGN analysis as well as the physical properties and thermodynamic data of Polyglycidyl nitrate.

### 2. Propellant Composition

Some researchers state the composition of solid propellants. Batchelder et al. [10] stated that the composition of the smokeless solid propellant for rocket propulsion is non-metallic solids and inorganic oxidizing salts ranging from 45% to 90%, unsaturated polyester resins from about 10% to 55%, and catalysts from 0.5% to 5%. The non-metallic solid compound and the inorganic oxidizing salt is ammonium perchlorate (AP). AP-based composite propellants have been in use for more than 50 years. This type of propellant usually contains AP embedded in the HTPB (hydroxyl-terminated polybutadiene) matrix [7]. The polyester resin contains condensation products in the form of diethylene glycol, adipic acid, and maleic anhydride, heteropolymer with n-butyl

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acrylate and methyl acrylate. The catalyst used is a mixture of about 1% to 50% ammonium dichromate and 50% to 99% alkyl ortho silicate. Hawkins and Campbell [11] discussed solid propellant formulas and their effect on combustion rates. The oxidizing agent used is ammonium perchlorate, Ammonium dinitramide (ADN) [12]. The addition of ammonium perchlorate in ammonium nitrate-based propellants will improve the performance of the propellant, especially burning rate, ignitability, and energy density [13]. Elrick and Gilbert [14] described a solid propellant composition containing an oxidizing agent, fuel, and binder in which the binder was cured with CTPB (carboxy terminated polybutadiene) mixed with diepoxide and triepoxide and a catalyst in the form of chromium 2-ethyl hexanoate. The CTPB composite was added with anti-oxidants to increase resistance to thermal oxidation [15].

Timnat [16] declared that modern propellants consist of oxidizing agents (70 to 80%), binders (10% to 20%), and metal additives (5% to 15%), while Willer and McGrath [17] stated that the solids content in the propellant ranges from 60% to 85% with a composition of the propellant binder of 20% to 40%, oxidizing agent of 55% to 80% and 1% to 2% of metal additives.

### 3. Propellant binders and their effect on propellant properties

There are two types of propellant binders, namely non-energetic polymers and energetic polymers. Examples of non-energetic polymers are Polycaprolactone (PCL), hydroxyl-terminated polybutadiene (HTPB) [18], polystyrene, and polypropylene glycol [19], Hydroxy-terminated Polyether (HTPE) [20].

Inert polymers can be used as propellant binders. HTPB (Hydroxy-Terminated PolyButadiene), PBAN (polybutadiene-acrylonitrile-acrylic acid terpolymer), PPG (polypropylene glycol), PEG (polyethylene glycol), polyester, polyacrylate, polymethacrylate, and CAB (Cellulose Acetate Butyrate) including inert polymer binders [21-22]. These binders have very good physical properties but their presence reduces the total energy output and reduces system performance.

Energetic polymers are polymers that generally contain energetic groups such as nitro, nitrate, azido, and others. The combustion products contain large amounts of nitrogen gas [23]. Various polymer compounds containing energetic functional groups such as azido groups (-N<sub>3</sub>), nitro groups (C-NO<sub>2</sub>), nitrate groups (O-NO<sub>2</sub>), nitro amino groups (N-NO<sub>2</sub>), and difluoroamino groups (N-F<sub>2</sub>) are promising as binders [24]. The polymers provide high energy during combustion, thereby significantly improving system performance. The binder also contains less carbon compared to conventional hydrocarbon elastomer binders so it is relatively environmentally friendly [23].

The polymers included in the energetic polymer binder category are nitrocellulose, PGN (polyglycidyl nitrate), and poly-NIMMO (poly (3-nitrate-methyl-3-methyloxetane)),

GAP (glycidyl acid polymer), 9DT-NIDA (diethylene glycol-triethylene glycol). -nitramino diacetic acid terpolymer), poly-BAMO (poly bis azido methyl oxetane), poly-AMMO (poly azido methyl-methyl oxetane), and poly-NAMMO (poly nitramino methyl-methyl oxetane) [21,25], BAMO and tetrahydrofuran (BAMO-THF) copolymers [26], poly-3-nitratomethyl-3-methyl oxetane (PNIMMO) and Ferrocene modified HTPBs [27], nitrated HTPB [28]. GAP and PNIMMO should be used as nitroformate-based hydrazinium propellants [25]. Non-energetic binders such as polyacrylates can be modified into energetic polymers [28]. Willer and McGrath [29] used a propellant binder of 12% to 60% by weight of the propellant.

The azido polymers that were first developed and included in the energetic polymer group were GAP and polyoxane such as poly-NIMMO. Min [30] stated that GAP-based propellants have shortcomings in terms of mechanical properties and low temperatures. The route of making GAP from epichlorohydrin to poly-epichlorohydrin which is then converted to GAP is a process that is not simple and requires relatively expensive reagents. Poly oxetane has mechanical properties that are not as expected, especially for rocket motor propellants. Another promising azido polymer is Poly-BAMO. Talawar et al. [24] explained that solidified Poly-BAMO could not be used as the propellant binder. Therefore poly-BAMO was copolymerized with THF (tetrahydrofuran). The copolymer has good mechanical properties but lower heat of formation than poly-BAMO.

Colclough et al. [31] expressed that the superior energetic polymers were PGN and poly-NIMMO. The results of the tests carried out stated that the two polymers in the propellant had very good properties and were not easily damaged. Both polymers contain oxygen-rich nitrate groups, making PGN and Poly-NIMMO a promising polymers [24]. The potential for PGN and poly-NIMMO can be seen from the relative value of the specific impulse which is far superior to the current composite [23].

Willer and McGrath [29] conducted another study on the performance of propellants with a composition of 12% to 60% propellant binder, 20% to 70% oxidizing agent, and additional metals (16% to 22%). The binders used are PBAN, HTPB, GAP, and PGN. The oxidizing agent that is often used is ammonium perchlorate (AP), the PGN binder used has the functionality of 2 or more and the hydroxyl equivalent weight ranges from 1000 to 1700, recommended between 1200 to 1600. The results are listed in Table 1 [29]. Table 2 shows that PGN has a theoretical specific impulse, at a pressure of 1000 psi which is expanded to 14.7 psi, which is higher than other polymers except for HTPB. The largest specific impulse value was obtained by using the PGN binder with the largest concentration. Meanwhile, the complete properties of propellants made using PGN binders are listed in Table 3. The use of additional metal in the form of aluminum in different amounts affects the properties of the resulting propellant. The larger the aluminum used, the smaller the stress, modulus, and burn rate, but the higher the value of strain, viscosity, density, and specific impulse with more aluminum.

**Table 1.** Specific impulse and propellant density with various types of propellant binders [29]

	PBAN	HTPB	GAP	PGN	PGN	PGN	PGN	PGN	PGN
Binder, %	14	12	30	30	30	30	30	30	30
oxidizer	AP	AP	AN	AN	AN	AN/HMX	AN/HMX	AN/CL <sub>2</sub> 0	AN/RDX
oxidizer,%wt	70	68	50	50	50	48	50	48	48
Al, %	16	20	20	20	22	22	20	22	22
Isp,lb-s/lb	262.0	265.3	259.7	259.6	260.7	264.0	262.4	263.9	264.0
Density, lb/in <sup>3</sup>	1.74	1.80	1.66	1.74	1.74	1.77	1.74	1.77	1.77

**Table 2.** Effect of PGN binder composition on propellant properties [29]

No	content, %			Viscosity, KP	Density, g/cm <sup>3</sup>	Specific impulse, lb-s/lb
	PGN	AN 200 $\mu$	AN 20 $\mu$			
1	30	50	-	96	1.62	254.0
2	60	20	-	8	1.59	254.2
3	35	25	20	14	1.60	252.8
4	30	30	20	64	1.62	254.0
5	35	25	19	18	1.61	251.1

**Table 3.** Propellant properties with PGN as a binder [29]

	Sample no. 6	Sample no. 7
Binder (PGN), %	30	30
Oxidizer (AN 200 $\mu$ ), %	50	50
Al, %	20	18
Stress, g/cm <sup>2</sup>	11881.811	14483.16
Strain, cm/cm	39	30
Modulus, psi	710	1100
Burn rate, 2000 psi, cm/s	0.84	1.04
Burn rate, 1000 psi, cm/s	0.53	0.64
Viscosity, KP	14	12
Density, g/cm <sup>3</sup>	1.731	1.707
Specific impulse, lb-s/lb	259.26	257.90

#### 4. Formation of polyglycidyl nitrate

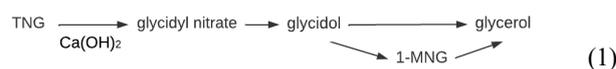
PGN is the result of a polymerization reaction with a monomer in the form of glycidyl nitrate. Glycidyl nitrate is synthesized from various reactants, i.e glycidyl tosylate [32], glycidol and nitrogen pentoxide [33-34], and epichlorohydrin [35]. These processes are not economically feasible for large-scale commercial production and are hazardous processes. and glycerol. Furthermore, Higsmit et al. [36] proposed a new route to obtain PGN from glycerol. This process is low cost and is a safe route to produce glycidyl nitrate of moderately high purity. Glycerol, mass yield around 10% [37], is a by-product in the biodiesel industry which will become waste if not utilized. Utilization of glycerol into PGN and other products will reduce waste and reduce production costs of these products. Glycerol can be processed into other products such as triacetin [38-39] and polyglycidyl nitrate [40].

There are three processes to make PGN from glycerol: nitration of glycerol, cyclization of 1,3-DNG, and polymerization of glycidyl nitrate [41]. Nitration of glycerol produces 1-MNG (1-mononitrolycerin), 2-MNG (2-mononitrolycerin), 1,3-DNG (1,3-dinitrolycerin), 1,2-DNG (1,2-dinitrolycerin) and TNG (trinitrolycerin). The main product of glycerol nitration is 1,3-dinitrolycerin (1,3-DNG). Nitration can be run in a batch process [36,42,43] or a continuous process [44]. The effect of temperature on the glycerol nitration reaction has been conveyed by Astuti et al. [45]. Kazakov et al. [46] reported that 7 reactions took place in the nitration of glycerol with nitric acid and the equilibrium constants for each reaction. The value of the equilibrium constant for the hydroxyl group located on the primary carbon atom in single-type compounds is much lower than for the secondary carbon atom [47]. Two nitronium ions form 1,3-DNG as quickly as both ions are available [48]. Secondary alcohols are relatively less reactive. An increase in the reaction temperature of benzene nitration will increase the

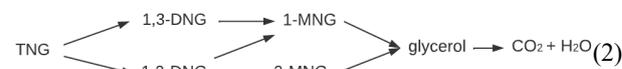
value of the rate constant for the reaction. The use of higher concentrations of nitric acid results in an increase in the rate constant. the rate of the benzene nitration reaction and a decrease in the activation energy [49].

Nitration consists of several reactions and is a reversible reaction. Under alkaline conditions, TNG will decompose. The reaction kinetics of a series, parallel, or series-parallel combination is following the stoichiometric coefficients of the reaction [50]. Nitration of benzene and some reactive compounds in sulfuric acid, chlorobenzene, toluene, dimethylbenzene and trimethylbenzene in trifluoroacetic acid, similar reactants in perchloric acid is a first-order reaction concerning each reactant [51-53]. Zaldivar et al. [54] have obtained pre-exponential factor and activation energy of toluene, benzene and chlorobenzene. Aburawi et al. [55] have proposed the activation energy of decomposition of nitroglycerine, 1,2-dinitrolycerine, and 1,3-dinitrolycerine. The decomposition was carried out at a temperature of 25 °C and at various pH (7.4, 10, 11, 13). The results showed that decomposition was slow at pH of 7.4, slightly faster under acidic conditions, and very fast under alkaline conditions. Decomposition at pH 13 is faster than decomposition at pH of 11. The use of lower concentrations of nitric acid causes the rate constant of the methanol nitration reaction to decrease [56].

In alkaline conditions, TNG will decompose. Kaplan et al. [57] stated the mechanism of TNG biodegradation as shown in Equation (1).



1-MNG is 1-mononitrolycerine. Furthermore, Christodoulatos et al. [58] presented another biodegradation mechanisms:



Aburawi et al. [55] also studied the reduction rates of TNG, 1,2-DNG, and 1,3-DNG at 25oC at various reaction times. Of the three compounds studied, it turned out that the decomposition of 1,2-DNG occurred the fastest, followed by the decomposition of 1,3-DNG. TNG compounds are the slowest to decompose. The decomposition of TNG produces 1,2-DNG, 1,3-DNG, and inorganic nitrate. The compound 1,2-DNG is converted to 1,3-DNG. The hydrolysis of 1,2-DNG to 1,3-DNG in a solution containing calcium hydroxide [58-59].

Several methods for quantitative analysis of nitrolycerin (TNG) compounds and their derivatives have been developed. These methods include gravimetry, titrimetry, electrochemistry, chromatography, and photometric techniques or the Schulze-Timan method. The

chromatographic method has been widely used since the 1960s and is a fast and reliable means of analysis. Several chromatographic techniques are used to determine the quantity of TNG in blood plasma and to analyze impurities in TNG compounds. Other methods have drawbacks. The Schulze-Timan method is a method with a long procedure, including extraction, evaporation, dilution, dissolving, and boiling. The gravimetric method requires the handling of dry nitroglycerin which has highly explosive properties. The titration method can only be used for solutions with a nitroglycerin content of at least 1%. Electrochemical methods can only be used to determine nitroglycerin compounds as well as gravimetric methods and titration methods [60].

Gas Chromatography (GC) is the instrument most often used to identify nitroglycerin compounds and their derivatives. Trowel [61] successfully identified mononitroglycerin, 1,3-DNG, 1,2-dinitroglycerin (1,2-DNG), and trinitroglycerin (TNG) in a double-base propellant using a GC equipped with a dual column with a flame ionization detector (FID). Test of lactose powder containing nitroglycerin with GC using dual FID detector and detecting retention time of nitroglycerin. The GC method is a simple and fast method with high precision and accuracy in determining sample quantity [62]. GC and HPLC methods are methods that can be used to analyze nitroglycerin in small samples. These methods have the advantage compare other methods: very sensitive, have a high level of accuracy, and selective [60].

The identification of nitrate esters and their derivatives was also carried out by Rosseel and Bogaert [63] with a dual column GC equipped with FID. Tests were carried out using two kinds of packed columns. This instrument can identify the retention times of all products of nitration, including in blood plasma [64-66]. Meanwhile, the characterization of 1,2-DNG and 1,3-DNG was studied by plasma assay using GCMS [67]. Quantification of the TNG concentration is quite effective using the capillary technique [64]. The stuffing column technique is sufficient for the identification of TNG, but it is difficult to detect and determine the quantity of TNG [64].

Calculation of concentration with GC can be done in three different ways, namely normalization, ESTD (ie quantitative method using standard solutions), and ISTD (ie quantitative methods using internal standard solutions). Internal standards are very useful for quantitative analysis of samples that are very difficult to control. There are various types of materials used as internal standards to identify TNG, 1,3-DNG, 1,2-DNG, 1-MNG, and 2-MNG compounds, including chloronitrobenzene [64], 2,4-dinitrotoluene [65], and o-iodobenzyl alcohol [65].

The peak area is the result of the integration of the mass per unit volume of the solute in the sample concerning time. In the internal standard method, the mass of a compound is calculated based on the ratio of the peak area of the compound to the peak area of a compound used as an internal standard. The mass fraction of compound G is expressed as [68]:

$$Fr_G = \frac{\text{berat standard} \times \text{area}_G \times \text{RRF}_G}{\text{berat sampel} \times \text{area}_{\text{standard}}} \times 100 \quad (3)$$

where: RRF = relative response factor

Blanco et al. [69] define the RRF value as the following equation:

$$RRF_i = \frac{A_r M_i}{A_i M_r} \quad (4)$$

Another equation that states the relationship between concentration and peak area is [70]:

$$C_i = C_{IS} K_{i/IS} \frac{A_i}{A_{IS}} \quad (5)$$

The definition of  $K_{i/IS}$  in the above equation is the same as the RRF proposed by Blanco et al. [69].

The RRF value depends on the compound being analyzed and the compound used as an internal standard. Based on mass percent and percent peak area, it is known that the RRF value of amide compounds ranges from 0.94 to 1.03 [71], and the RRF value of 2,2 tetrachlorodibenzo-p-dioxins ranges from  $0.74 \pm 0.07$  to  $1.26 \pm 0.11$  [72], and the RRF of 57 of aromatic polycyclic compounds detected using FID by split injection was in the range of 0.793 to 1.130 [69]. Costin et al. [73] used the term total correction factor (TCF) to express RRF. They searched for TCF for 27 kinds of sterol compounds and the results stated that the TCF for these compounds ranged from 0.9841 to 1.0 [73].

Modeling the kinetics of the glycerol nitration reaction involves 7 reactions that occur in nitration [40]. A simpler model is constructed by assuming that there are 3 reactions in the nitration of glycerol [40]. The 3-reaction model is more in line with the experimental data than the 7-reaction model. The optimum conditions for the glycerol nitration reaction are the reaction temperature of 20°C, the mole ratio of nitric acid/glycerol 5/1, and the concentration of nitric acid of 69% [74-75].

The second stage of the reaction for the manufacture of polyglycidyl nitrate from glycerol is the cyclization of 1,3 dinitroglycerin to glycidyl nitrate. Cyclization can be carried out in batches [36] or continuously [44] using vessels and decanters, in inorganic hydroxides such as sodium hydroxide, potassium hydroxide, and lithium hydroxide [42], with the solvent methylene chloride. The concentration of sodium hydroxide solution ranges from 25 to 50% [36]. According to Highsmith and Johnston [44], the cyclization reaction can be carried out at a temperature of 0 to 25°C, preferably at 24°C. The results of 1,3-DNG cyclization prepared with variations in glycerol weight, sodium hydroxide weight, sodium hydroxide content, and temperature [36]. The optimum conditions for dinitroglycerin cyclization are the temperature of 288.15 K and the mole ratio of sodium hydroxide /glycerol of 1.5 [75]. Glycidyl nitrate can also be obtained from other raw materials, namely glycidyl tosylate [32], glycidol, and nitrogen pentoxide [33-34,76], epichlorohydrin, a mixture of 60% HNO<sub>3</sub> solution, KNO<sub>3</sub>, and 20% NaOH solution [35].

Epoxide formation is an exothermic reaction [77]. Ring epoxides are unstable and susceptible to heat in aqueous solutions. The activation energy depends on the electronegativity of the heteroatom, the force constants, and the strain energy of the ring formed.

The third step is the polymerization of glycidyl nitrate to form polyglycidyl nitrate. The reactions that occur include the type of cation polymerization with a polyol initiator and an acid catalyst [36,78]. Acid catalysts are boron trifluoride, boron tetrafluoride, triethyl oxonium hexafluorophosphate, boron trifluoride etherate, boron trifluoride tetrahydrofuran, BF<sub>3</sub>, PF<sub>5</sub> and SbF<sub>5</sub> gases [78-80]. This reaction uses an organic solvent such as dichloroethane or dichloro methane so that it belongs to the category of solution polymerization method. The mechanism of the polymerization reaction has been described by previous researchers [8,31,76,78].

## 5. Physical properties and thermodynamic data of Polyglycidyl nitrate

Isotactic PGN is a solid compound with a melting point of 47.2°C [32]. From the separation process by evaporation, a pale yellow thick liquid PGN was obtained [36]. The molecular formula of PGN can be seen in figure 1.

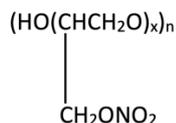


Fig. 1. molecular formula of PGN

The atactic PGN was created by Ingham and Nichols of the Jet Propulsion Laboratory. They found that PGN prepared with a boron trifluoride etherate catalyst had low functionality (<2) and an average molecular weight of 1500. The polyurethane propellants prepared from PGN had poor mechanical properties [80]. The presence of the NO<sub>3</sub>- group increases the O balance during combustion and causes the energetic nature of PGN [80].

Willer et al. [79] attempted to obtain PGN polymers with isotactic branch chains with two or more hydroxyl

functionalities. The average molecular weight of the theoretical weight (M<sub>w</sub> theory) ranges from 2470 to 3696, while the M<sub>w</sub> based on GPC (Gel permeation chromatography) ranges from 1020 to 4726. The theoretical molecular weight is determined by adding the molecular weight of the initiator in the product obtained by dividing grams of monomer per mole of the initiator. M<sub>w</sub> and M<sub>n</sub> were determined by GPC using a polystyrene calibration standard with 4 series columns from 100 to 100,000 amsrong. The hydroxyl equivalent weight was determined by the anhydride titration method and NMR end group analysis. The values are 1000 to 1700, preferably about 1200 to 1600. Willer et al. [81] stated that the molecular weight of PGN was measured by GPC, the value of M<sub>n</sub> (mean molecular weight) was 2231, M<sub>w</sub> was 2644 and M<sub>w</sub>/M<sub>n</sub> was 1.19. According to Diaz et al. [22], the M<sub>n</sub> value is 1700 and the M<sub>w</sub> value is 2100. Sanderson and Martins [42] used NMR to calculate M<sub>n</sub>. Desai et al. [76] stated that PGN is soluble in energetic plasticizers such as metriol trinitrate. The physical properties of PGN from various studies are stated in Table 4, each researcher obtained different PGN M<sub>n</sub> and M<sub>w</sub> values. While the values of density, viscosity, glass transition temperature, melting temperature, and O<sub>2</sub> balance are almost the same.

Table 4. Physical properties of PGN

Ref.	M <sub>n</sub> , g/mol	M <sub>w</sub> , g/mol	ρ, g/cm <sup>3</sup>	μ, poise	T <sub>g</sub> , °C	T <sub>m</sub> , °C	f	O <sub>2</sub> balan- <i>ce</i> , %
[79]	646 s.d 4474	2472 s.d 3698	n/a				≥ 2	n/a
[81]	2231	2644	n/a			47,2		n/a
[76]	3000	4400	1.39	46 (50°C), 163 (30°C)	-35	n/a	≤ 2	n/a
[35]								
lab scale	n/a	1800 s.d 3000	1.43	n/a	-32	n/a	n/a	n/a
scale-up	n/a	4600 s.d 4900			-34	n/a	n/a	n/a
[82]	1000 s.d 3000	n/a	1,42	163 (30°C)	-35	n/a	n/a	n/a
[8]	n/a	n/a	1,46	n/a	-35	n/a	~ 2	-60.5
[22]	1700	2100	n/a	n/a	n/a	n/a	n/a	n/a
[42]	5370	n/a	n/a	n/a	n/a	n/a	n/a	n/a
[43]	5370.4	n/a	n/a	n/a	n/a	n/a	n/a	n/a
[24]	n/a	n/a	1.39	n/a	-35	n/a	n/a	-61
[83]	n/a	n/a	1.39	n/a	-35	n/a	n/a	-61

The other properties of PGN are presented in Table 5. Impact sensitivity is the most important characteristic of energetic materials in terms of storage and handling. The sensitivity to PGN collisions is 25 KJ. Provatas [8] stated that the sensitivity of PGN is too low to be included in class 1 explosives (UK classification). PGN's ignition temperature of 170°C indicates that PGN is not flammable.

Table 5. Other physical properties of PGN

Ref.	Properties	lab scale	scale-up
[3 5]	decomposition by DSC, 10°C/min (°C)	>188	>194
	OH index (eq/kg)	0.67 s.d	0.58 s.d
		0.80	0.63
	Vacuum thermal stability (mL/g)	0,4	0,4

[8]	Sensitivity to impact (kJ)	25	25
	Hydroxy Value (mg KOH/kg)	~37	n/a
	Suhu penyalaan, °C	170	n/a

The thermodynamic data of glycidyl nitrate and PGN in the form of heat of combustion, the heat of formation, heat of reaction, heat of the explosion, and heat capacity are known, shown in Table 6. According to Provatas [8], H<sub>expl</sub> PGN was 2661 kJ/kg, higher than GAP and poly-NIMMO (2500 and 818 kJ/kg). This proves that PGN is more energetic than GAP and poly-NIMMO. PGN's heat of combustion and heat of reaction is high, so safety is an important factor in the process with PGN.

Table 6. Thermodynamics data of PGN

Ref.	PGN					Glycidyl nitrate	
	C <sub>p</sub> , J/kg.K	ΔH <sub>c</sub> , kJ/kg	ΔH <sub>f</sub> , kJ/mol	ΔH <sub>R</sub> , kJ/mol	ΔH <sub>expl</sub> , kJ/kg	C <sub>p</sub> , J/kg.K	ΔH <sub>R</sub> , kJ/mol
[35]	1425,6	n/a	n/a	603,7	n/a	3,195	614,7
[8]	n/a	n/a	-284,5	n/a	2661	n/a	n/a
[22]	n/a	-14700	-5691*	n/a	n/a	n/a	n/a

[24]	n/a	n/a	-285	n/a	n/a	n/a	n/a
[83]	n/a	n/a	-285	n/a	n/a	n/a	n/a

\*data:  $\Delta H_f = -2,71$  kJ/g,  $M_w = 2100$  g/mol

Colclough et al. [31] compared the physical properties of PGN and other energetic polymers. A comparison of these properties can be read in Table 7. HTPB is a potential material but has problems related to stability related to the presence of side reactions and how to control operating conditions to produce the desired product. Therefore, PGN synthesis is a priority for research on energetic polymers. Table 7 shows

that Mn PGN is relatively low compared to other polymers. The highest energy level and density of PGN with a glass transition temperature of  $-35^\circ\text{C}$ . This indicates that PGN has enormous potential as a propellant binder [31]. PGN's viscosity is low enough to facilitate handling in the laboratory and during processing.

**Table 7.** Properties of various energetic polymers [31,84]

	$M_n$ (GPC)	$\rho$ , g/cm <sup>3</sup>	$\mu_i$ , poise	$T_g$ ( $T_m$ ), °C	$O_2$ balance, %*	exotherm maximum, °C	Functionality, OH	$\Delta H_f$ , kJ/kg
poli BAMO	2000 s.d 7000	1,3	n/a	-39 (+61)	-123.8	227	2	2460
GAP	500 s.d 5000	1.2	50	-40 (n/a)	-121.2	212	1.5 s.d 2	957
Poli-NIMMO	2000 s.d 15000	1.26	1350	-25 (n/a)	-114.3	229	2 s.d 3	-309
PGN	1000 s.d 3000	1.42	163	-35 (n/a)	-60.5	222	2 s.d 3	-284
NHTPB	2500	1.20	128	-58 (n/a)	n/a	206	4 s.d 3.8	-442

Storage, handling, and transportation of PGN require data on several PGN properties such as solubility, stability at ambient temperature, resistance to shock and heat, flash point, and reactivity to other compounds such as acids and bases. However, PGN's material safety data sheet is not yet available so these properties are approximated by those of nitroglycerin (see Table 8).

**Table 8.** PGN Properties Approach of Nitroglycerin

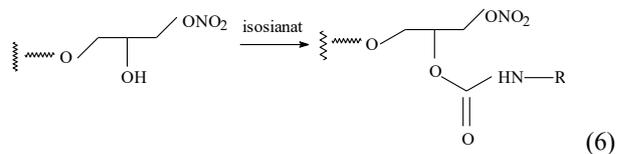
Properties	Information
solubility	water-soluble Soluble in energetic plasticizers such as metriol trinitrate [76]
Stability	Stable
Conditions to avoid	heat, contact with an ignition source
materials to avoid	acid, oxidizer

PGN is a very viscous polymer so it must be cured or crosslinked with di and/or polyfunctional isocyanates to obtain elastomeric binders for solid propellants [81]. Examples of aromatic diisocyanates are toluene diisocyanate, phenylene diisocyanate, and/or methylene di-p-phenylene diisocyanate [42]. However, Provatas [8] stated that the uncured PGN prepolymer had good chemical stability, if cured with isocyanate it produced less stable polyurethane rubber. Accelerated aging results in rubber degradation. Degradation cannot be prevented with stabilizers except oxygen.

Elastomer that undergoes cross-link treatment (Cross-link elastomer) when used as a binder has drawbacks. The cross-linking of the elastomer must be carried out for a short period called the "pot life". The burning of cross-link elastomers creates environmental problems. Some thermoplastic elastomers fail to be used in the preparation of propellant formulations because the process must be carried out below  $120^\circ\text{C}$ . The thermoplastic elastomer used as a binder should have a melting point between  $40$  and  $120^\circ\text{C}$ . If the temperature is below  $40^\circ\text{C}$  and during storage, there is an increase in temperature, then the propellant composition softens. This is not desired. If the temperature is above  $120^\circ\text{C}$ , then there is an increase in temperature, then some components of the propellant, especially oxidizable particles,

and energetic plasticizers are unstable. Therefore, the expected PGN is a solid crystalline material that can be used as a hard block of thermoplastic elastomer-based PGN [32]. According to Sanderson et al. [85] thermoplastic, elastomeric polymers should have a melting point between  $60$  and  $120^\circ\text{C}$ .

The curing process will increase the hardness of the polymer. The following equation (6) shows the curing reaction of PGN with isocyanates [42]:



The hardness (Shore A hardness) of PGN after curing with toluene diisocyanate was measured periodically. The results are listed in Table 9 and compared with PGN that was cured with aliphatic isocyanates. It is recommended that the reduction in hardness is not more than 10% for 24 days of measurement. Ideally, there is no decrease in hardness over the measurement period [42]. Table 9 shows that the decrease in hardness with the toluene diisocyanate curing agent is lower than that with the aliphatic isocyanate.

**Table 9.** PGN hardness after being cured with toluene diisocyanate

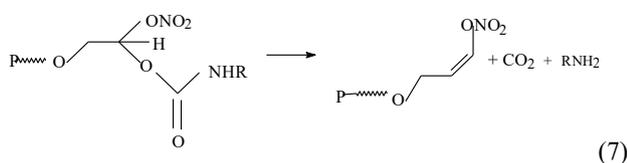
Day	Hardness, dimensionless	
	Toluene diisocyanate	Aliphatic isocyanate
1	77	68
3	82	62
7	n/a	58
8	76.5	n/a
10	80	n/a
11	n/a	56
14	n/a	52
15	82.6	n/a
17	78.6	n/a
21	n/a	51
24	81	42

The curing process with PAPI (polyaromatic polyisocyanate such as polymethylene polyphenyl isocyanate) was stated by [43], listed in table 10. The curing process was carried out at a temperature of 62.8°C. The observations in Table 10 show that the hardness of PGN after being incubated for 13 days was relatively stable. Hardness reduction is less than 10%.

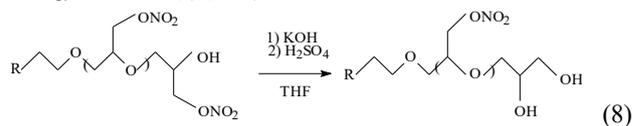
**Table 10.** PGN's hardness after being cured with PAPI [43]

day	hardness
6	60
13	63
20	65
27	65
41	64

Provatas [8] declared that instability is a problem associated with PGN pre-polymers, and does not depend on the use of isocyanates. The problem was solved by modifying the chain end to give the pre-polymer PGN diol termination as shown in Equation (7).



Paraskos et al. [86] proposed another method for the final modification of PGN using a single solvent. Equation (8) shows the result of the final modification of PGN in the form of a stable crosslinked polymer with aliphatic polyisocyanate.



## 6. Conclusion

Solid propellants are preferred over liquid propellants because they have several advantages in various aspects, including in terms of manufacture, ability to store energy and drive force of rocket. There are two types of solid propellants, namely homogeneous propellants, and heterogeneous propellants. Homogeneous propellants that are widely developed are three-component-based propellants containing oxidizing components, binders, and additives. There are two kinds of propellant binders, namely non-energetic polymers and energetic polymers. Energetic polymers are preferred because the specific impulse value and combustion rate are higher than non-energetic polymers, and can increase the density and combustion temperature. PGN is a very promising energetic polymer. The specific impulse value of propellant with PGN binder is proven to be higher than the use of PBAN, HTPB, and GAP. The use of additional metals such as Aluminum affects some of the properties of the propellant. PGN can be made from glycerol which is a waste of the biodiesel industry. There are 3 steps to obtain PGN from glycerol, i.e nitration of glycerol to 1,3-DNG, cyclization of 1,3-DNG to glycidyl nitrate, and polymerization of glycidyl nitrate to PGN.

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