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Probing the Compatibility of Energetic Binder Poly Glycidyl Nitrate with Energetic Plasticizers: Thermal, Rheological and DFT Studies

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Abstract: The essential idea of developing energetic binders and plasticizers is to enhance the thermal stability and energy content, improve the oxygen balance and burning behaviour of moulds, reduce the glass transition temperature and improve other mechanical properties of the propellant and explosives formulations. The compatibility of energetic binder poly glycidyl nitrate (PGN) with some energetic plasticizers of solid propellants was studied by using the differential scanning calorimeter (DSC), rheology and DFT methods where it deals with the effect of addition of five different energetic plasticizers i.e. bis (2, 2-dinitro propyl) acetal (BDNPA), dinitro-diaza-alkanes (DNDA-57), 1,2,4-butanetriol trinitrate (BTTN), N-N-butyl-N'(2-nitroxy-ethyl) nitramine (BuNENA) and diethyleneglycol dinitrate (DEGDN) on the rheological and thermal properties of energetic binder PGN. The results obtained for the mixture of plasticizer and binder in the parameters of decomposition temperature (T_{max}) and the format of the peak are compared with the results obtained for the pure binder indicating the compatibility of these plasticizers with PGN. Glass transition temperature (T_g) of all these mixes were determined by low temperature DSC and showed lowering of T_g with single peak. Rheological evaluation revealed that the viscosity of the binder is sufficiently lowered with the increase in flow behaviour on addition of 20% (w/w) plasticizer. The addition of 20% DEGDN has maximum effect on the lowering of viscosity of PGN.

Quantum chemically derived molecular electrostatic potential (MESP) shows the possible sites of interaction of plasticizers and binder with the estimated deepest V_{\min} values and their magnitudes provide an insight for their mutual interactions. The relative trend of interaction energies between plasticizer and binder PGN is well correlated with the corresponding trend of ability of plasticizers towards reducing the viscosity of PGN. The information gathered in the present work would in general be valuable to design new plasticizers as a prior.

Keywords: Thermal, Glass transition temperature, Rheology, Plasticizing effect, Computational study.

1 Introduction

The combination of three branches viz. explosives, propellants and pyrotechnics was named by a generic term ‘high energy materials’ (HEMs) or energetic materials (EMs). High energy materials are fascinating and exceptional for both academic and general interest due to their tremendous impact on the economy and industries and their innumerable applications in almost all walks of life in addition to the different military applications. The obligations of HEMs for civil solicitations are growing every time with the annual increasing rate of 8 – 9%. The considerable amounts of civil or commercial explosives are being used for gold mining and other metal mining in countries like South Africa, USA, Canada and Sweden. The mainstream applications of blasting explosives are in mining, quarrying and other important civil application of HEMs includes civil engineering works such as tunnel driving, road building, canal construction, land reclamation. Large quantities of explosives have also been employed in seismographic prospecting for new oil fields which involves drilling a hole into the solid rock or coal, inserting cartridge of explosive with a detonator followed by firing of explosive to fracture and bring down the rock or coal bed. Further, commercial HEMs are being employed for miscellaneous applications in automobile industries as an ingredient of automotive safety airbags in vehicles, in food industry for the manufacture of self-heating food cans, in metallurgy for metal cladding and welding.¹

An explosive is a chemical compound or mixture of compounds which when suitably initiated undergoes very rapid exothermic and self-propagating decomposition with the formation of more stable products. Propellants are low explosives which by their regularity of burning produce large volume of gases at high temperature and pressure. As a result of combustion occurs in the chamber of a gun or rocket motor, projectile is accelerated to very high velocity transforming the chemical energy into kinetic energy. Pyro-technique is essentially an art of creating complex and heterogeneous fire using highly energetic and sensitive mixtures of inorganic and organic compounds in order to meet the requirements of military for special effects like illumination, delay, smoke, sound and incendiary etc. Though, the term HEM is new to general audience, energetic materials are generally organic compounds containing nitro, azide and hydrazino groups in the molecules. These materials produce energy by a regular process of chemistry called oxidation with sudden release of energy when undergo decomposition.²

It is well known that the use of high energy materials in their pure form is very rare; rather most of the energetic materials (RDX, HMX, CL-20 etc.) are used in conjunction with the inert (HTPB, DOA etc.) as well as other energetic materials (GAP, PLN etc.) in high explosive and propellant formulations. One of the major ingredients of propellant and explosive compositions is polymeric binder which generally requires a small quantity of plasticizer for its processing. Currently, hydroxy-terminated polybutadiene (HTPB) is in use and have excellent elastomeric properties. However, it contains little energy and requires high solid loading, *i.e.* percentage of filler, to have a sufficient performance.³ The use of such conventional polymers for explosive and propellant formulations brings down the overall energy of such systems.⁴ Also, due to sensitive nature of oxidizer there are problems related to processing and vulnerability at very high solid loadings. Therefore, to reduce the vulnerability without lowering the performance, energy can be added to the explosive or propellant system through the use of energetic binder which enables lowering the solid loading or maintaining the same solid loading with enhanced performance.^{5,6}

This is the genesis of the energetic binder that come into the picture. The use of an energetic binder, *e.g.* GAP (poly glycidyl azide), allows for lower solid loading, but have dissatisfactory mechanical properties like tensile strength, % elongation, initial modulus and hardness.⁷ The polar groups in the molecular structure of this compound rendering it to increase viscosity and elevate their glass transition temperatures. The rise in glass transition temperature downgrades the low temperature characteristics, which is especially important for missile propellants. The design of insensitive explosives and weapons will decrease the likelihood of unexpected and unwanted detonation from external stimuli such as shock, weapon fragments and heat. This can be achieved with the necessary modifications of the weapon system, the explosive formulation or a combination of both. One of the most successful methods would be the use of insensitive energetic binder ingredients, where the explosive components are bound together by a polymeric binder, forming a rubbery composition which is less susceptible to shock and other stimuli.⁸ Poly glycidyl nitrate (PGN) has emerged as a most promising energetic binder for insensitive munitions and of worth investigating.^{4,7} Since, the performance of any energetic binder mainly depends on its ability to contain maximum solid ingredients like crystalline explosives, solid loading of more than 80% is always preferable for the development of various munitions. In order to achieve the solid loading of more than 80% in case of PGN, it is always recommended to plasticize the composition with suitable plasticizer. Various types of plasticizers can be used for this purpose but the choice of suitable or compatible plasticizer often become difficult for the processing as well as for the end use of the composition. A plasticizer is usually defined in terms of the desired properties of a given polymer/plasticizer system.⁹ Plasticizer changes the properties of formulations by reducing stiffness and permitting easier processing to impart a desirable degree of flexibility over a broad range of operational temperatures and lowers the temperature at which the material becomes brittle. To obtain a high specific impulse, it is desirable to use optimum energetic plasticizers which have a low glass transition temperature, a

low viscosity, a low ability to migrate, a high oxygen balance and also it should be thermally stable.¹⁰

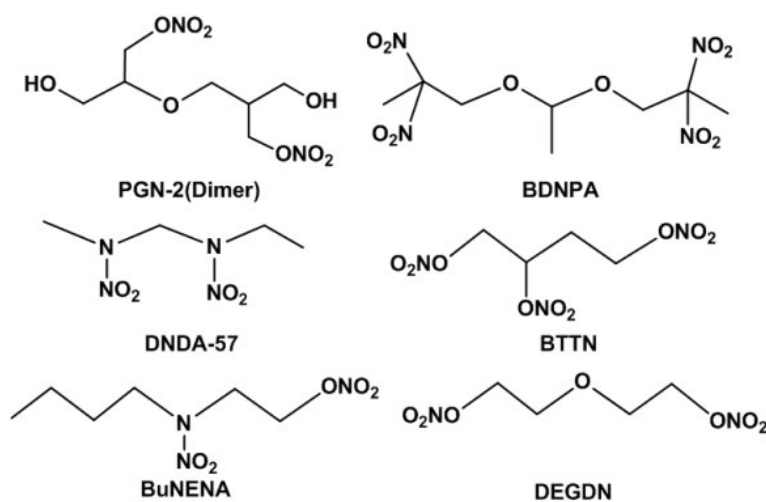


Chart 1 Molecular structures of energetic binder poly glycidyl nitrate (dimeric form) and all energetic plasticizers.

Compatibility testing of ingredients of explosives and propellant compositions is to ensure safety during storage and reliability in services by determining whether its properties are adversely affected by any of the materials used near or in contact with them.¹¹ Inert plasticizers, *e.g.* DOA (dioctyladipate), can be used to circumvent these problems, but the addition of an inert component will increase the demands on the solid loading. Therefore, energetic components are preferred. Hitherto, the known energetic plasticizers have inconveniences such as low thermal stability, low energy content, high migratory ability, and sometimes dissolution of the filler. The low thermal stability can be remedied with stabilisers, but finding a molecule which is stable as such is a very interesting area of research. Nitrate esters are important plasticizer in nitrate ester plasticized polyether (NEPE) propellants and other double-based propellants. Incorporating nitrate ester plasticizer into propellant formulations can improve their mechanical properties at low temperature and make them safer to use.¹²⁻¹⁵ Experimental studies using thermal and rheological^{16,17} techniques as well as computational studies at molecular level¹⁸ may be of useful to understand the compatibility of PGN binder with different plasticizers (Chart 1) which includes nitrate esters as

well as nitramine class and also to get better insight for selection of suitable plasticizer. Therefore, the present paper deals with the rheological behavior of the PGN blended with different type of energetic plasticizers in terms of shear viscosity in order to make the compositions processable with better solid loading.

2 Methodology

2.1 Experimental

For the synthesis of PGN, reactants like epichlorohydrin (Loba Chemie), sodium hydroxide (Ranbaxy, AR), nitric acid (Rankem 70%), 1,4-butane diol (99% Fluka), BF_3 etherate (48%, Fluka), sodium chloride (Rankem), sodium sulphate (anhydrous, Rankem), sodium bicarbonate (Ranbaxy, AR), potassium nitrate (Qualigens, AR), dichloromethane (Rankem) were used as received from the trade without further purification. The structure of the intermediates, monomer and the final polymers were studied using ^1H NMR spectra recorded on a Bruker-300 MHz instrument using tetra methyl silane (TMS) as an internal reference and CDCl_3 as solvent. IR spectra were recorded on a Perkin Elmer FT-IR 1605 spectrophotometer by smear method. UV-Vis spectra were recorded on a GBC make cintra 10e UV-Vis spectrophotometer by using acetonitrile as solvent (concentration 1mg/ml). The purity of the compound was determined by Dionex Ultimate 3000, high performance liquid chromatography (HPLC) at a flow rate of 1ml/min. Polymeric properties such as molecular weight, both number average and weight average as well as the polydispersity was determined by GPC. PGN was synthesized in two steps based on the lines of the reported method.^{19,20} This method involves the synthesis of the monomer followed by its polymerization (Scheme 1).

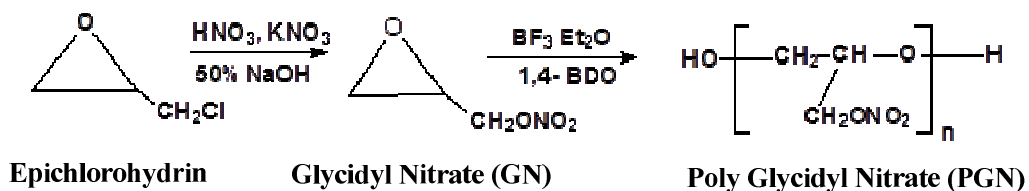
(a) Synthesis of Glycidyl Nitrate (GN)

To a three necked round bottom flask fitted with condenser, stirrer and dropping funnel, nitric acid (50 ml, 60%) and potassium nitrate (30.3g, 0.3 mol) were added. The reaction temperature of the contents was maintained at 10°C and epichlorohydrin (92.5 g, 1mol) was added

drop wise over a period of 3 hrs by keeping the temperature in the range 8-12 °C. To the above reaction mixture, 50% aqueous sodium hydroxide (112g) was added at 5 °C over a period of 3 hrs and left for overnight at room temperature. The organic layer was extracted with dichloromethane (50ml × 2) and washed with water (100ml × 2). Then it was dried over anhydrous sodium sulphate (20g) and dichloromethane (100ml) was removed under vacuum. The obtained GN was purified by distilling at 45 °C under reduced pressure (5mm of Hg). Yield: (36g, 30%).

(b) Synthesis of Poly Glycidyl Nitrate (PGN)

Dichloromethane (10 ml) was taken in a 250 ml three necked bottom flask to which BF₃ etherate (3.55g, 0.025 mol), 1, 4 butane diol (BDO) (1.12g, 0.0125 mol) were added at 20 °C and stirred for 30 min in nitrogen atmosphere. Glycidyl nitrate (59.5g, 0.5 mol) in 40 ml dichloromethane was then added to the above solution drop wise for 3 hrs maintaining the temperature at 13±2 °C. The reaction mixture was stirred at room temperature for 24 hrs. The polymerization reaction was terminated with brine solution and the polymer was extracted with dichloromethane. It was washed with aqueous sodium bicarbonate solution, water and dichloromethane (DCM) solvent containing PGN was dried over anhydrous sodium sulphate. The polymer (PGN) was precipitated by adding cold methanol (~10 °C) to DCM solution and dried under vacuum at 50 °C. Yield: (47.5g, 80%).



Scheme 1 Synthesis of glycidyl nitrate (GN) and poly glycidyl nitrate (PGN).

All the characterization data for GN and PGN have been appended in the electronic supplementary information (ESI†). Similarly, synthetic procedures for the plasticizers along with

the reaction schemes and the characterization data have been provided as the electronic supplementary information (ESI†).

When using DSC as a technique to determine the compatibility, the results obtained for the pure product in the parameters of decomposition temperature and the glass transition temperature are compared with the results obtained for the binder/plasticizer mixtures. If the peak related to mixture moves for temperatures lower than the peak related to the energetic material or the material in test, indicates incompatibility. The incompatibility degree is measured by the difference of temperature among the peaks. PGN was synthesized in two steps namely the synthesis of monomer, Glycidyl nitrate (GN), followed by its polymerization as per the reported methods.^{19,20} Energetic plasticizers viz. bis (2, 2-dinitro propyl) acetal (BDNPA),^{21,22} dinitro-diaza-alkanes (DNDA-57),²³ 1,2,4-butanetriol trinitrate (BTTN),^{24,25} N-N-butyl-N'(2-nitroxy-ethyl) nitramine (BuNENA)²⁶ and diethyleneglycol dinitrate (DEGDN)^{24,25} were also synthesized and characterized in lab by reported methods. Other chemicals and reagents used in this study were received from the trade and used as such. All the energetic plasticizers (20% w/w) were hand mixed with PGN (80% w/w) and kept for 24 hrs at room temperature. After 24 hrs, these blends were observed for any phase separation and then used for further studies as discussed in results and discussion section. DSC samples (weight between 5 to 10 mg) were sealed in an aluminium pan. Thermal decomposition and glass transition temperatures of all the polymer blends were determined using Perkin Elmer DSC (DSC-7) in the temperature range of -60°C to 400°C with a constant heating rate of 10°C min⁻¹ under nitrogen atmosphere. T_g was determined as the intersection of the low temperature side of the baseline with the tangent through the inflection associated with the rising heat capacity. A stress control Rheometer (Model-Stress Tech, Rheologica instruments AB, Sweden) was used to measure the dynamic and steady shear tests. The instrument is equipped with 20 mm diameter parallel plate (20 ETC) at gap of 0.5 mm. The steady shear data were collected from shear rate sweep from 1 to 100

/s. All experiments were carried out at a constant temperature of 30°C. A pre-shear period, 30 second, was used to standardize the handling of samples before measurement.

2.2 Computational

For the computational studies, all the geometries were fully optimized by employing popular Becke three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) method^{27,28} in conjunction with 6-311(d,p) basis set. Such type of methods has already been employed in the other works where intermolecular interactions play role.²⁹⁻³¹ Harmonic frequency calculations at the same level of theory were used to characterize the stationary points as minima and to provide thermal and zero point corrections. Single-point calculations were performed at the B3LYP/6-311G(d,p) level to generate Molecular Electrostatic Potential (MESP) surfaces in gas phase. All quantum chemical calculations were performed using Gaussian 09, Revision C.01 program.³² MESP surfaces have been generated with Gauss View 5.0 suit of program. The interaction energy (ΔE_i^\ddagger) model is a powerful tool to explain the reactivity in bimolecular reactions.³³ By definition, interaction energy is $E_{\text{Inter}} = E_{\text{Blend}} - (E_{\text{Binder}} + E_{\text{Plasticizer}})$. The MESP was calculated using eq (1) where Z_A is the charge on nucleus A, located at R_A and $\rho(r')$ is the electron density.³⁴

$$V(r) = \sum_A^N \frac{Z_A}{|r - R_A|} - \int \frac{\rho(r') d^3 r'}{|r - r'|} \quad (1)$$

In general, electron dense regions are expected to show high negative MESP whereas electron deficient regions are characterized by positive MESP.³⁵⁻⁴⁰ The most negative valued point (V_{min}) in electron rich regions can be obtained from the MESP topography calculation.⁴¹⁻⁴³

3 Results and discussion

3.1 Thermal studies

Differential scanning calorimeter (DSC) was performed to see any change in decomposition pattern of binder entity with and without plasticizer. In order to study the plasticizing effect of given plasticizers on PGN binder through thermal studies, DSC analysis was carried out in terms of glass transition temperature (T_g) and thermal decomposition temperature (T_{max}) on binder and on binary mixtures of binder/plasticizer. The properties of the PGN are given in Table 1. Mol. Wt. (M_n) was found to be 2484 with a viscosity of 5174 cPs at 30°C. PGN decomposes exothermically at 214°C with a heat output of 2859 J/g as revealed by DSC.⁴⁴ To study the compatibility of energetic plasticizers with energetic binder PGN, all the plasticizers under consideration were mixed with the binder thoroughly. The plasticizer content in propellant compositions can be varied from 0 to 35 wt % of the pure polymer. However, we have considered binder/plasticizer mixture at a ratio of 80:20 (w/w) as suggested in the literature.⁴⁵⁻⁴⁷ After through mixing of 20% of various energetic plasticizers to the PGN (80%) binder separately, resultant mixtures were kept at room temperature for 24 hrs or more to observe any phase separation. No layer separation or any other sign of heterogeneity has been observed indicating the physical compatible of studied energetic plasticizers with PGN binder. The decomposition peak profiles of DSC analysis shown in Fig. 1 and the corresponding peak temperatures (T_{max}) are summarized in Table 2.

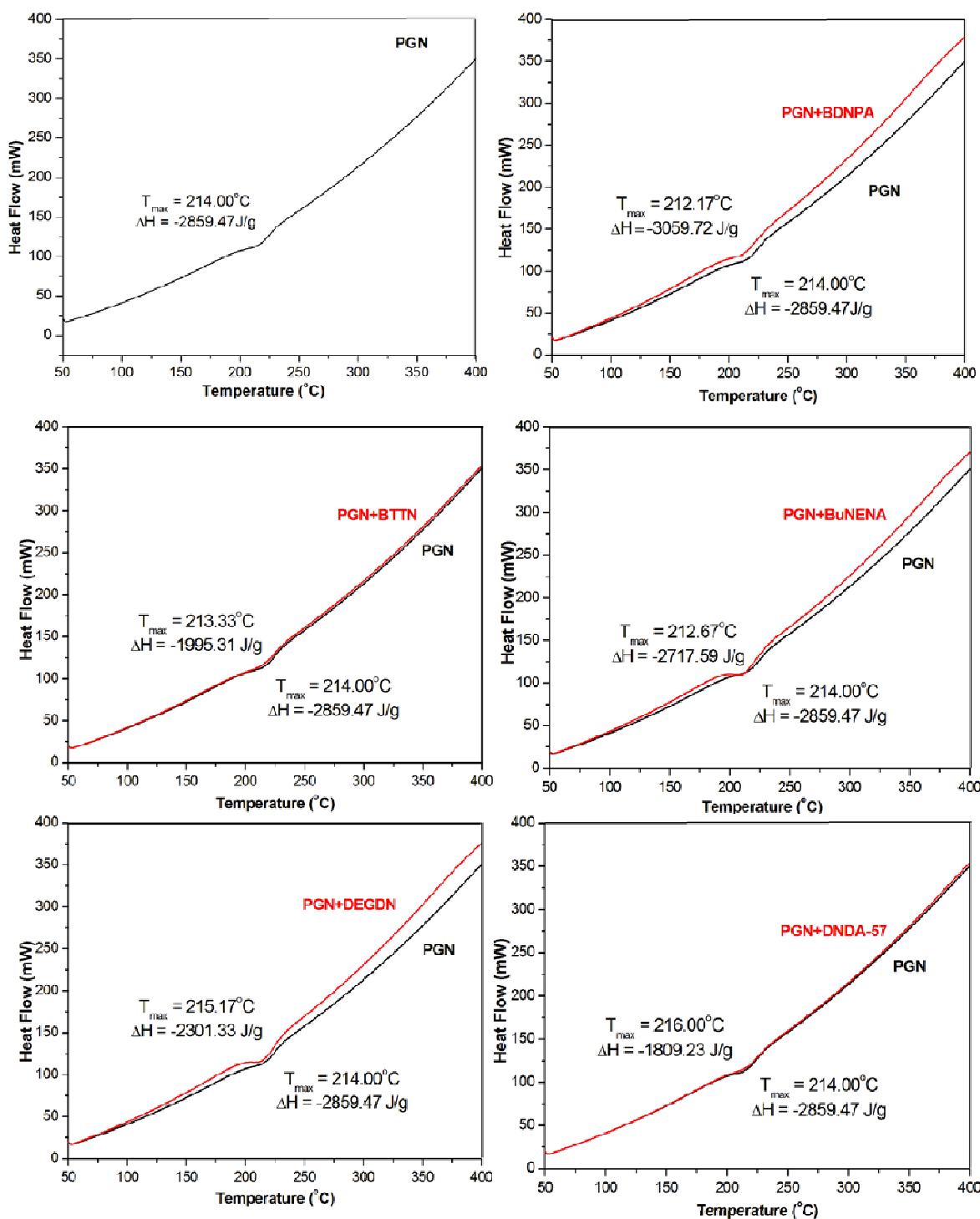


Fig. 1 DSC curves (Heat flow endo up vs temperature) of pure PGN and PGN mixed with different plasticizers.

The DSC curve of PGN shows the main decomposition process in the temperature range of 195–225 °C with only one exothermic peak temperature at 214 °C, where the complete gas products

are formed. From the thermal profile of DSC, (Table 2) it is found that the decomposition temperature (T_{\max}) i.e. 214°C, is not effectively altered by the addition of 20% of energetic plasticizer in all the cases. Therefore, characteristic temperatures of decomposition remain practically unchanged when the plasticizer was added. Consequently, all the plasticizers can be considered to be compatible with PGN when safety is concerned. The decomposition energy of PGN decreases with the addition of plasticizers. However, in the case of BDNPA, the increase in the decomposition energy has been observed. It is hypothesized that polar interactions between the carbon and the nitrate ester group strain the labile O–NO₂ bond and result in lower decomposition temperatures of carbon bound nitrate esters. The amount of shift in the decomposition temperature of the nitrate ester is dependent on the strength of the interaction between binder and plasticizer.⁴⁸ The evaluated standards of compatibility for explosive and contact materials are listed in Table 3.^{49,50} The decomposition of PGN is almost consistent by the addition of plasticizers with the minimal exothermic peak variation in the range 212°C to 216°C. According to the standards of compatibility^{49,50} evaluated in Table 3, it is concluded that all the binary systems viz. PGN/BDNPA, PGN/BuNENA, PGN/BTTN, PGN/DEGDN and PGN/DNDA-57 have the deviation of ≤ 2 °C from decomposition temperature (T_{\max}) (Table 2). DSC curves of such binary systems suggest that there is an acceptable effect on the decomposition process of binder and mixture of binder/plasticizer. Therefore, the lack of new peaks, no alteration in the peak format and the similar decomposition peak temperatures with and without plasticizer indicates the compatibility of PGN with studied energetic plasticizers.

Table 1 Properties of Poly Glycidyl Nitrate (PGN).

SNO	Properties	PGN
1	\bar{M}_n	2484
2	Viscosity (cPs)	5174
3	T_g (°C)	-34.95
4	ΔH_f (J/g)	-2859
5	T_{\max} (°C)	214

Table 2 Effect of Different Plasticizer Addition on Glass Transition Temperature (T_g) and Decomposition Temperature (T_{max}).

SNO	PGN + 20% Plasticizer	T_{max} (± 0.7 °C)	T_g (± 0.7 °C)
1	PGN	214.00	-34.95
2	PGN + BDNPA	212.17	-44.91
3	PGN + DNDA-57	216.00	-51.20
4	PGN + BTTN	213.33	-39.38
5	PGN + BuNENA	212.67	-53.01
6	PGN + DEGDN	215.17	-45.24

Table 3 Evaluated Standards of Compatibility for Explosives and Contacted Materials

SNO	Deviation from T_{max}	Rating	Description
1	≤ 2	A	Safe for use in any explosive formulation
2	3 – 5	B	Safe for testing purpose in a short period of time
3	6 – 15	C	Not recommended for use with explosive items
4	> 15	D	Hazardous. Should not be used at any condition

The glass transition occurs when movement of molecules in the system is restricted due to low temperature at which the binder changes from rubbery to brittle. The phenomenon of plasticization results from the addition of a diluent (called *plasticizer*) to a polymer in which it is miscible in all proportions so as to lower the resultant glass transition temperature (T_g). Considerable data have been produced for the effect of monomer mixture on the T_g 's of copolymer systems have appeared in the literature.⁵¹⁻⁵⁶ The T_g of a number of polymer and plasticizer mixtures at various polymer-to-plasticizer ratios were determined. The molecular flexibility of the plasticizer is an important mechanism for altering the brittleness of polymers via plasticization. From a practical point of view, the implication of this observation can be obtained from the T_g measurements. Herewith, all the plasticizers were used to reduce the T_g of PGN and to increase the processibility of the binder/plasticizer blend. The effect of plasticizer addition was observed in terms of lowering of T_g of PGN which again tells about the compatibility of plasticizers with PGN. Maximum lowering of T_g (-53.01°C) is found in the case of BuNENA (Fig. 2). While BDNPA,

DNDA-57 and DEGDN gives T_g at -44.91°C , -51.20°C and -45.24°C respectively, BTTN has shown minimum lowering of T_g at -39.38°C . The single point T_g values for all combinations is the evidence of the presence of single phase homogeneous system which confirms the thermodynamic compatibility of energetic binder with energetic plasticizers.^{45,55,56} All these PGN/Plasticizer blends shown reduced glass transition temperatures as observed by low temperature DSC, which also confirms the compatibility of PGN binder with the plasticizers. This is due to the reduction in cohesive forces of attraction between polymer chains as plasticizer introduces free volume in the material and, like any solvent, promotes polymer–plasticizer interactions at the expense of polymer–polymer interactions.⁵²⁻⁵⁴ Possibility of low barriers for segmental motion of the polymer backbone when plasticizers are added to polymer significantly reduces the resultant brittleness. Such weak barriers depend strongly on the chemical structure of the polymer backbone, side groups and intermolecular forces between polymers and plasticizers imparting reduction in glass transition temperature (T_g) of blend. Therefore, BuNENA/PGN and DEGDN/PGN blends shows maximum lowering of T_g due the presence of weak interactions with polymer backbone as compared to all other plasticizer/binder blends.

Based on these desirable characteristic properties of BuNENA/PGN and DEGDN/PGN blends, it is proposed that BuNENA and DEGDN seems to be the best suitable plasticizers for PGN in order to achieve maximum solid loading and better processing. However, the ability in lowering of T_g , having T_{max} values within the standards of compatibility makes the other three plasticizers BDNPA, BTTN and DNDA-57 also suitable as potential plasticizers for energetic binder PGN. The development of a theory for the prediction of composition-dependent glass-transition temperatures for multi-component mixtures which manifest single glass transitions is of some fundamental interest and, moreover, has practical merit in connection with their processing conditions and in-service properties.

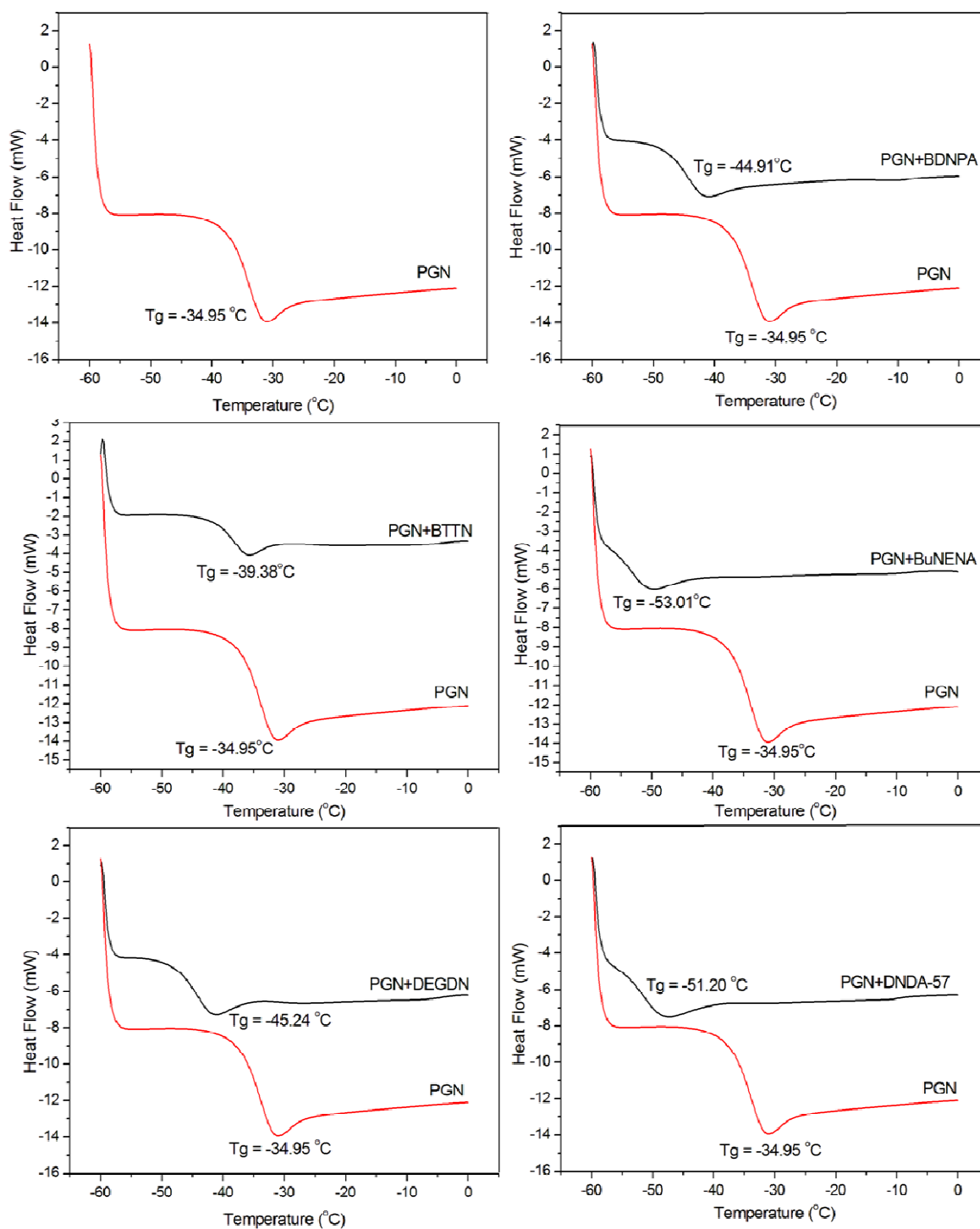


Fig. 2 Low temperature DSC curves of pure PGN and PGN mixed with different plasticizers.

3.2 Rheological studies

Compatibility of a polymeric binder with plasticizer is possible when both together form homogeneous system. The maximum amount of a plasticizer incorporated into a polymeric binder

and retained by it without oozing out during storage is known as the limit of compatibility.⁵⁷ The mechanical properties of the binder are altered by the addition of a plasticizer, which imparts the rubbery characteristic that is required for insensitive munition, reduces the viscosity for ease of casting and enables higher solids loading. To study the compatibility of energetic binder PGN with all the five plasticizers, the samples prepared for above thermal studies were also subjected to rheological studies.⁵⁸ The ability of the plasticizers to lower the viscosity of the polymer was measured on 80:20 mixtures of PGN and plasticizer as considered in the thermal studies. In order to study the flow behavior in terms of viscosity of PGN and PGN/plasticizer blends, shear rate sweep (Fig. 3) from 1 to 100 S^{-1} was performed at constant temperature of 30 °C. Newtonian behavior has been observed for pure PGN with a constant viscosity of 5174 cPs, at a varying shear rate. Such a viscosity of pure PGN is too high to consider it for solid loadings more than 50% (w/w). After addition of 20% (w/w) energetic plasticizers, it has been observed that the viscosity of binder/plasticizer blend has reduced drastically along with increase in flow behavior. Although quantity of the plasticizer added to the binder is fixed, the mixes showed different flow behavior by means of viscosity. The addition of DEGDN imparts maximum effect in reducing the viscosity up to 897 cPs from 5174 cPs, (Fig. 3). Similar effect is observed with other plasticizers also, but not up to the same extent. The ability of the plasticizers BDNPA and DNDA-57 to lower the viscosity of the polymer PGN was measured to be 2850 cPs and 2220 cPs respectively. It was shown that BuNENA and BTTN were effective in lowering the viscosity of PGN to 1260 cPs and 1570 cPs respectively. Since, polymer is the major component in a typical polymer/plasticizer system; it is possible to use viscosity of dilute polymer solutions as measure of the solvent power of the liquid for the polymer. Liquids with high solvent power for the polymer cause a stretching out of the chain molecules, whereas a liquid of poor solvent power causes the segments of the polymer chain to stay close to each other leading to coil up. Hence, viscosity measurements are used to obtain information about the degree of coiling of the chain molecules and therefore, about the solvent power of the

plasticizer for the polymer. Thus, it is the plasticizer's role to reduce the forces between the macromolecules and thereby increase chain mobility, flow behavior etc. which in turn leads to a 'softening' or "plasticization" of the polymeric materials. The above behavior of any plasticizer depends on polarity, size (molecular weight) and shape (linear/branching) of plasticizer molecules. Therefore, different plasticizers behave differently in the given polymer. DNDA-57 is a nitramine class of plasticizer and it contains two $-NNO_2$ groups, whereas there are four $-CNO_2$ groups in BDNPA chemical structure as it belongs to nitro class of plasticizers. Similarly, DEGDN and BTTN belong to nitrate class of plasticizers since they contain two and three $-ONO_2$ groups, respectively. BuNENA belongs to nitrate-nitramine class which contains both $-ONO_2$ and $-NNO_2$ groups. Consequently, the relative ability of plasticizers towards reducing the viscous nature of resultant mixture (binder/plasticizer) may be anticipated in the increasing order of $BDNPA < DNDA-57 < BuNENA < BTTN < DEGDN$. Therefore, DEGDN ranks first in reducing the viscosity because it causes loose binding interactions between segments of polymeric binder PGN.

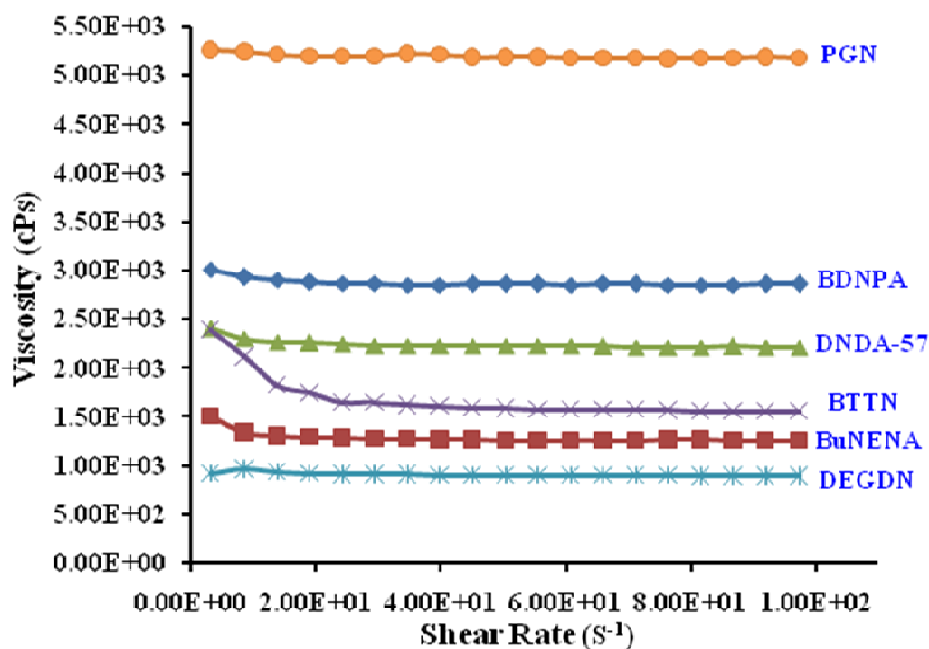
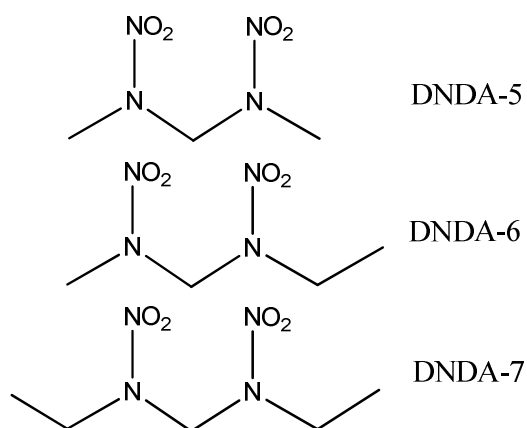


Fig. 3 Shear rate sweep test of PGN and PGN mixed with different plasticizers (20% w/w).

3.3 DFT studies

To obtain the maximum mechanical property benefit from this polymer system, the polymeric networks must be physically compatible with the energetic plasticizer molecules. Therefore, an understanding of the interaction between polymer and plasticizer is essential. In order to understand the compatibility of energetic polymeric binder PGN with different energetic plasticizer molecules and the factors responsible for the resultant flow behavior of binder/plasticizer mixtures, we have attempted for quantum chemical calculations employing DFT method at B3LYP/6-311G(d,p) level of theory. As in the experimental study, we have considered all the five energetic plasticizers viz. DNDA-57, BuNENA, DEGDN, BTTN and BDNPA. The chemical structures and the corresponding optimized geometries of these plasticizers are depicted in Chart 2. Initially, we have optimized plasticizer molecules at B3LYP/6-311G(d,p) level to get stable conformers. To minimize the computational effort for the electronic structure calculations, Model compounds whose structures resembled the terminal branches of actual compounds were considered for two molecules. They are: 1) Polymeric binder PGN which is modeled with its dimeric form. 2) DNDA-57 plasticizer is a mixture of three homologue compounds viz. DNDA-5, DNDA-6 and DNDA-7 (Scheme 2). DNDA-5 has two methyl groups as its terminals whereas DNDA-7 has two ethyl groups as its terminals. We have considered DNDA-6 in our computational study since it may be the best simulant of DNDA-57 as it contains both methyl and ethyl groups at its terminal positions in order to study the compatibility of DNDA-57 with PGN. Henceforth, we will refer DNDA-6 as DNDA-57 for the purpose of comparison with experimental findings. The stable forms of binder and plasticizers obtained through optimization have been considered for the examination of their mutual compatibility via molecular electrostatic potential (MESP) and inter-molecular interaction studies.



Scheme 2 Chemical structures of components of DNDA-57 plasticizer.

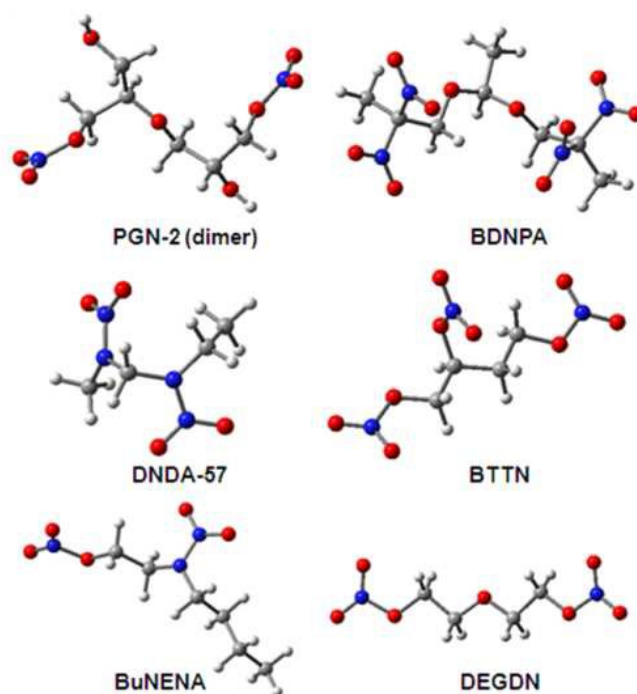


Chart 2 Optimized geometries of PGN-2(dimer) and energetic plasticizers at B3LYP/6-311G(d,p) level. (grey: carbon; red: oxygen; blue: nitrogen; white: hydrogen).

Initially, we have generated the MESP surfaces for dimeric PGN binder and the five plasticizer molecules to identify possible site of interactions spread over them. MESP is an important aspect and have been widely used topographical quantity for understanding molecular reactivity, coarse guess about intermolecular interactions, molecular recognition, electrophilic

reactions, substituent effects etc.³⁵⁻⁴³ MESP analysis gives the most negative valued potential point (V_{\min}) in electron rich regions obtained through topography calculations in any molecular system (Fig. 4). It is obvious that the plasticizers will show possible locations of V_{\min} nearby respective explosophores (-NNO₂/ $-CNO_2$ / $-ONO_2$). From Table 4, it is clear that the V_{\min} of nitro ($-CNO_2$) group is more negative than that of nitrate ($-ONO_2$) group. It is also clear that V_{\min} of nitramine ($-NNO_2$) is even more negative than that of nitro ($-CNO_2$) group. From this, it is deduced that plasticizers containing nitramine group may have higher reactive tendency towards PGN than the plasticizers which contains nitro and nitrate groups. However, the binding ability of plasticizers further depends on number of such explosophores. BDNPA and BTTN should possess more number of site of interactions with four and three explosophores, respectively whereas BuNENA, DNDA and DEGDN contains only two site of interactions as they possess two explosophores each. The total V_{\min} due to all the explosophore groups present on each plasticizer are in the decreasing order of: BDNPA > DNDA-57 > BuNENA > BTTN > DEGDN. According to this total MESP- V_{\min} trend, the relative interactive trend of plasticizer should also be the same. Generally, reduced viscosity of resultant polymer matrix can be obtained as a result of weak or loose intermolecular interactions. Consequently, the relative ability of plasticizers towards reducing the viscous nature of resultant mixture (binder/plasticizer) may be anticipated in the increasing order of BDNPA < DNDA-57 < BuNENA < BTTN < DEGDN. Therefore, DEGDN ranks first in reducing the viscosity because of its loose binding nature towards segments of polymeric binder. However, it is difficult to predict the reactivity trend of plasticizers on the basis of MESP- V_{\min} values solely when intermolecular interactions between binder and plasticizer play role. Therefore, we have considered the binder and plasticizers for the study which involves intermolecular interactions in order to understand the compatibility of plasticizers with binder.

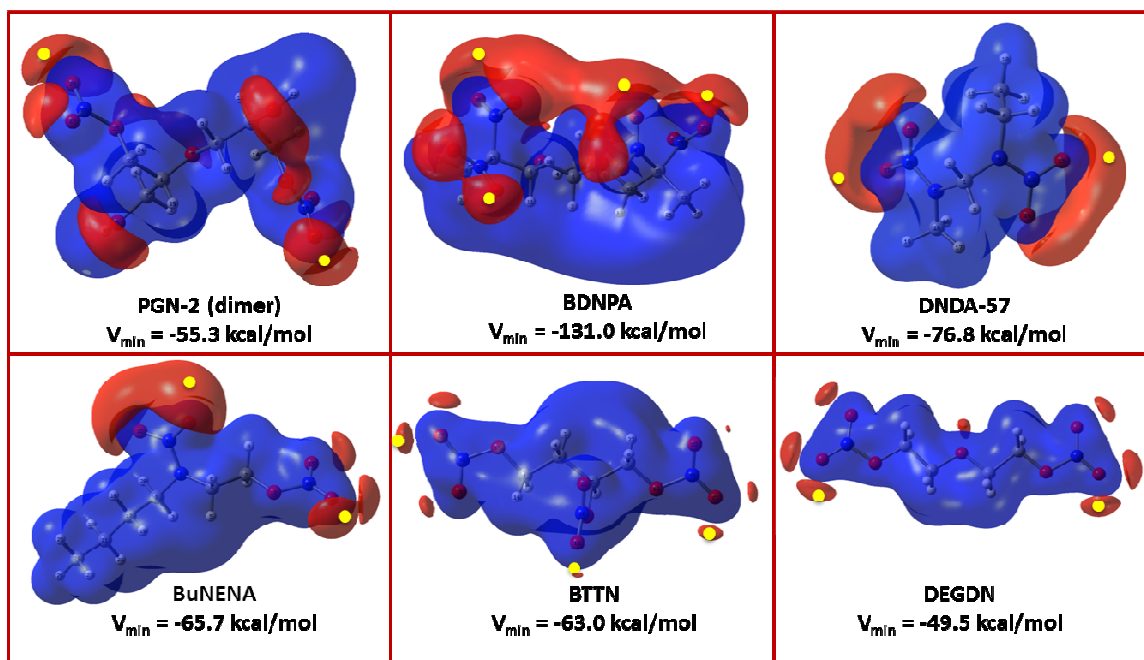


Fig. 4 MESP surfaces generated for PGN dimer and energetic plasticizers at B3LYP/6-311G(d,p) level along with the corresponding total V_{\min} of explosophores. The yellow dot represents the location of the V_{\min} point in each explosophore. (red: electron rich regions; blue: electropositive regions).

Table 4 All Possible V_{\min} Values (kcal mol^{-1}) for Plasticizers Available for Interaction with Binder.

SNO	Molecule	$V_{\min} (-\text{NNO}_2)$	$V_{\min} (-\text{CNO}_2)$	$V_{\min} (-\text{ONO}_2)$	Total V_{\min}
1	PGN	-	-	-28.0, -27.3	-55.3
2	BDNPA	-	-36.6, -32.5 -30.8, -31.1	-	-131.0
3	DNDA-57	-38.5, -38.3	-	-	-76.8
4	BTTN	-	-	-22.5, -19.2 -21.4	-63.0
5	BuNENA	-40.5	-	-25.2	-65.7
6	DEGDN	-	-	-24.7, -24.7	-49.5

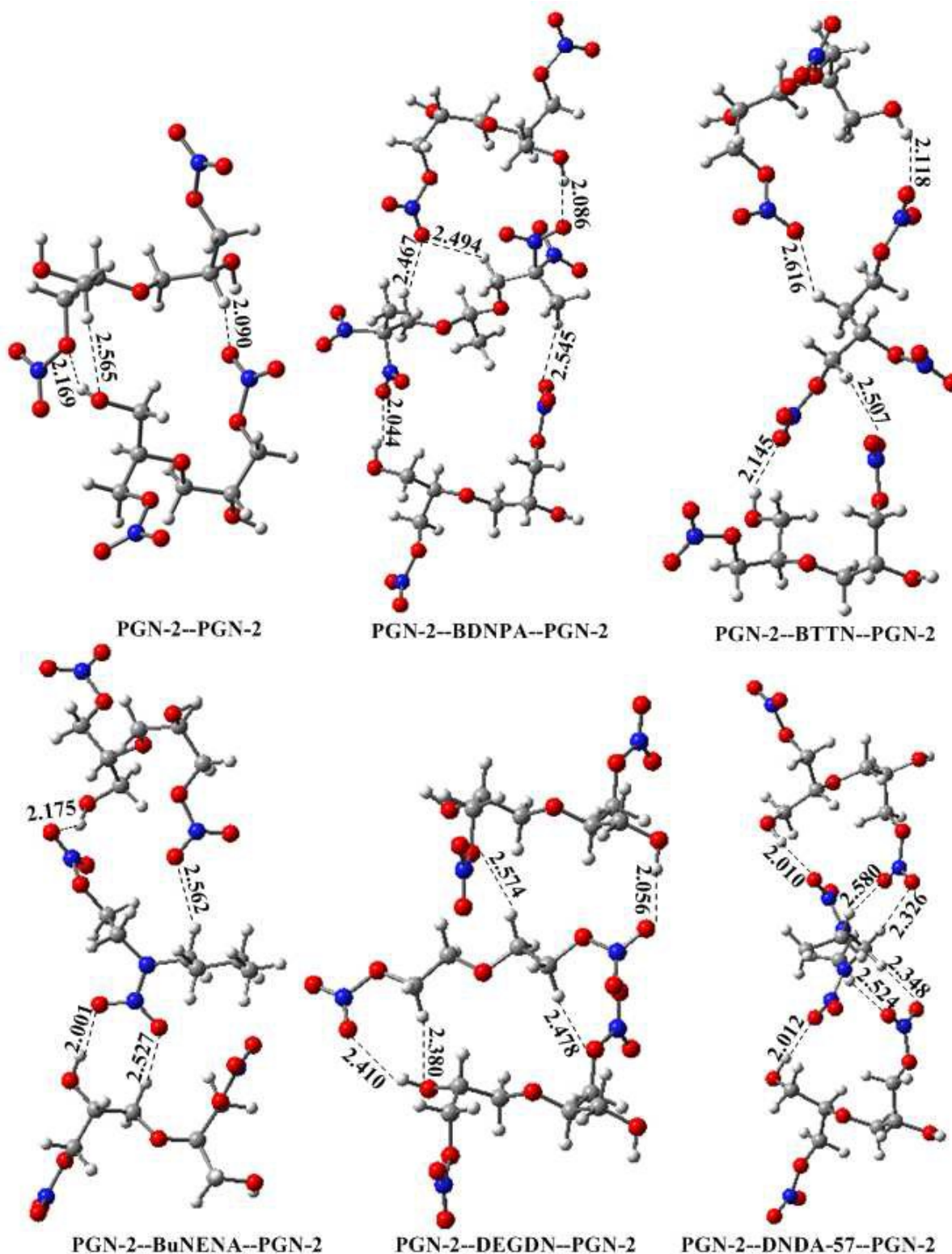


Fig. 5 Optimized geometries of adducts of two segments of PGN dimer and energetic plasticizer at B3LYP/6-311G(d,p) level. (grey: carbon; red: oxygen; blue: nitrogen; white: hydrogen).

Initially, we have carried out the studies on the interactions of plasticizer with one segment of PGN-2 (Details are provided in ESI). Now, the interactions of plasticizer with two segments of PGN-2 have been explored, taking into account several different geometries of interaction. The optimized structures of adducts between two PGN-2 segments and plasticizer as the models of binder/ plasticizer system are presented in Fig. 5 along with the resultant inter molecular interactions indicated with dotted lines. In all cases, optimization of various starting geometries converge to different interaction types, in which the plasticizer molecule is oriented by the NO₂ group or by the C–H groups in between two binder fragments. The computed intermolecular distances and free energies reveals that the molecular C–H groups play the main role in the interaction of plasticizer which is oriented mainly by the C-H groups towards two segments of PGN-2. In this study, the two fragments of PGN-2 forms a complex with BDNPA through three -C-H···O- type of interactions (2.467 Å, 2.545 Å and 2.494 Å) and two -O-H···O type hydrogen bonding interactions at a distances of 2.044 Å and 2.086 Å. Complex of two molecules of PGN-2 with BTTN involves two -C-H···O- type of interactions (2.616 Å and 2.507 Å) and two -O-H···O (2.118 Å and 2.145 Å) type hydrogen bonding interaction. Complex of PGN-2 and BuNENA consist of two H-bonds (2.175 Å and 2.001 Å) and two weak -C-H···O- type of interactions (2.527 Å and 2.562Å). Similarly, the distances 2.580 Å, 2.326 Å, 2.348 Å and 2.524 Å are corresponding to -C-H···O- type of interactions whereas 2.010 Å and 2.012 Å is corresponding to -O-H···O interaction of H-bonding in the case of DNDA-57. DEGDN shows three -C-H···O- interactions (2.574 Å, 2.478 Å and 2.380 Å) and two -O-H···O type interactions (2.410 Å and 2.056 Å) as observed in the case of BDNPA. The electronic interaction energies (kcal mol⁻¹) for the formation of the complex of PGN-2 with different plasticizers viz. BDNPA, DNDA-57, BTTN, BuNENA and DEGDN were found to be – 11.2, –10.8, –8.8, –7.6 and –2.8, respectively (kcal/mol, Table 5). The computed interaction energy results in terms of electronic and Gibbs free energies suggest that BDNPA prefers to interact more strongly with PGN-2 whereas DEGDN has less interaction as compared to all other plasticizers

(Table 5). Computed results show that the interaction trend of plasticizers varies at DNDA-57 and BTTN in the study of single fragment (PGN2-plasticizer) as compared to the theoretical MESP trend and experimental viscosity trend. However, the computed interaction energy trend of adducts of PGN2–plasticizer–PGN2 was found to be well matched with V_{\min} trend of MESP analysis and experimental viscosity trend. Therefore, the interaction ability of plasticizers predicted using two segments of PGN-2 may be of more sensible and necessary to mimic the plasticizer introduction between the polymeric segments of binder. It would be even more realistic if one can consider the higher number of polymer segments. However, we have restricted our modeling studies to two polymeric segments to avoid increasing number of atoms which requires expensive computational power.

Generally, a homogeneous phase is obtained because of the existence of specific favorable interactions between polymer and plasticizer components, which allow mixing on a molecular scale. One such favorable interaction is hydrogen bonding between polymer/plasticizer blends. Polymers such as PGN, containing nitrate (ONO_2) groups, are proton acceptors due to the basic nature of the functional groups. At the same time, PGN carries two proton-donating hydroxyl groups at the chain ends causes $-\text{C}-\text{H}\cdots\text{O}-$ type of interactions with plasticizer. In practice, the plasticization effect involves often the specific interactions or excess volume formation upon mixing the polymer and plasticizer, which lead to the negative T_g deviations. As per the interaction energies reported in the Table 5, the plasticizers BuNENA and DEGDN causes weak interactions (due to less number of functional groups) with polymer backbone as compared other plasticizers which are well correlated with the fact that these plasticizers shown maximum reduction in glass transition temperature of experimental thermal studies as mentioned in section 3.2.

Table 5 Electronic and Gibbs Free Energies (kcal/mol) for Interaction between Plasticizers and Binder (PGN-2).

SNO	Plasticizer	Electronic energies		Gibbs free energies	
		One segment	Two segments	One segment	Two segments
1	PGN-2	-	-11.7	-	4.3
2	BDNPA	-14.3	-11.2	3.7	5.2
3	DNDA-57	-11.6	-10.8	2.9	6.3
4	BTTN	-11.9	-8.8	6.4	6.9
5	BuNENA	-8.2	-7.6	5.1	9.8
6	DEGDN	-6.4	-2.8	7.5	13.9

4 Conclusions

Compatibility of PGN with energetic materials in propellants or explosives is most important aspects of PGN in practical application. However, investigations on these aspects are rarely reported. Therefore, this study is to investigate the interactions and compatibilities between PGN and some common energetic plasticizers. The effects of addition of five different energetic plasticizers viz. BDNPA, DNDA-57, BuNENA, BTTN and DEGDN in the energetic binder PGN have been studied in detail employing thermal, rheological and computational techniques. It has been observed that all the five plasticizers are compatible with the energetic binder PGN as there was no phase transformation. The lowering of glass transition temperature (T_g) has been seen in all the cases. Among all the five plasticizers, BuNENA lowers T_g to a maximum extent (-53.0°C) whereas BTTN lowers to minimum extant (-39.4°C). Similarly, maximum increase in flow behavior (lowering of viscosity) has been observed by the addition DEGDN whereas minimum increase in flow behavior by BDNPA. The relative ability of plasticizers towards reducing the viscosity of resultant plasticizer/binder blend is in the increasing order of BDNPA < DNDA-57 < BuNENA < BTTN < DEGDN. Such relative ability of energetic plasticizers for energetic binder PGN has been explained on the basis of intermolecular interactions employing density functional calculations using the magnitudes of Gibbs free energies and electronic energies of interaction. All the five

plasticizers BuNENA, DEGDN, BDNPA, BTTN and DNDA-57 were found suitable/compatible for energetic binder PGN. Moreover, it has been observed that DEGDN and BuNENA shown more potential towards PGN.

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Supporting Information

Cartesian coordinates of all the optimized stationary points at B3LYP/6-311G(d,p) in the gas phase, including corresponding charge and multiplicity were given.

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Graphical Abstract**Probing the Compatibility of Energetic Binder Poly Glycidyl Nitrate with Energetic Plasticizers: Thermal, Rheological and DFT Studies**Sujit Kumar Shee^a, Sreekantha T. Reddy^a, Javaid Athar^a, Shaibal Banerjee,^{b,*}M. B. Talawar,^a Arun Kanti Sikder^{a,*} and Md Abdul Shafeeuulla Khan^{a,*}^a *Energetic Materials Research Division, High Energy Materials Research Laboratory (Defence Research & Development Organization), Pune, India-411 021.*^b *Defence Institute of Advanced Technology (Defence Research & Development Organization), Girinagar, Pune - 411 025, India.**Correspondence to: SB (shaibal.b2001@gmail.com), MASK (maskhan@hemrl.drdo.in)