RSC Advances

PAPER

Cite this: *RSC Adv.*, 2015, **5**, 101297

Probing the compatibility of energetic binder poly-glycidyl nitrate with energetic plasticizers: thermal, rheological and DFT studies†

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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 propellant and explosives formulations. The compatibility of energetic binder poly-glycidyl nitrate (PGN) with some energetic plasticizers of solid propellants was studied using differential scanning calorimetry (DSC), rheology and DFT methods in relation to the effect of the 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 the energetic binder PGN. The results obtained for the mixture of plasticizer and binder with respect to 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. The glass transition temperatures (T_g) of all these mixes were determined by low-temperature DSC, which showed a lowering of T_g with a single peak. Rheological evaluation revealed that the viscosity of the binder is sufficiently lowered with an increase in flow behaviour on addition of 20% (w/w) plasticizer. The addition of 20% DEGDN has the maximum effect on the lowering of the viscosity of PGN. Quantum chemically derived molecular electrostatic potential (MESP) shows the possible sites of interaction of plasticizers and binder with the estimated lowest V_{min} values and their magnitudes provide an insight into their mutual interactions. The relative trend in interaction energies between plasticizer and binder, PGN, is well correlated with a corresponding trend in the ability of plasticizers towards reducing the viscosity of PGN. The information gathered in the present study would in general be valuable with respect to designing new plasticizers.

Received 15th August 2015
Accepted 9th November 2015

DOI: 10.1039/c5ra16476a

www.rsc.org/advances

1 Introduction

The combination of three branches of science, *viz.* explosives, propellants and pyrotechnics, was given the generic term, 'high energy materials' (HEMs) or energetic materials (EMs). High energy materials are interesting both generally and academically due to their tremendous impact on the economy and industries and their innumerable applications in almost all walks of life, in addition to different military applications. The uses of HEMs in civil applications are growing continuously with an annually increasing rate of 8–9%. Considerable amounts of civil or commercial explosives are being used for gold mining and other metal mining in countries such as South Africa, USA, Canada and Sweden. The mainstream applications of blasting explosives are in mining and quarrying and other important civil applications of HEMs include civil engineering work such as tunnel driving, road building, canal construction and land reclamation. Large quantities of explosives have also been employed in seismographic prospecting for new oil fields, which involves drilling a hole into solid rock or coal, inserting a cartridge of explosive with a detonator, followed by firing of explosive to fracture and bring down the rock or coal bed. Furthermore, commercial HEMs are being employed for miscellaneous applications in the automobile industry as an ingredient of automotive safety airbags in vehicles, in the food industry for the manufacture of self-heating food cans and in metallurgy for metal cladding and welding.[1]

An explosive is a chemical compound or mixture of compounds, which when suitably initiated, undergoes very

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† Electronic supplementary information (ESI) available: Cartesian coordinates of all the optimized stationary points at B3LYP/6-311G(d,p) in the gas phase, including corresponding charge and multiplicity, are given. See DOI: 10.1039/c5ra16476a

rapid exothermic and self-propagating decomposition with the formation of more stable products. Propellants are low explosives, which by their regularity of burning, produce a large volume of gases at high temperature and pressure. As a result, if combustion occurs in the chamber of a gun or rocket motor, a projectile is accelerated to very high velocity, transforming the chemical energy into kinetic energy. Pyrotechnics is essentially the art of creating complex and heterogeneous fire using highly energetic and sensitive mixtures of inorganic and organic compounds in order to produce special effects such as illumination, delay, smoke, sound and incendiary. Although the term HEM is new to the general audience, energetic materials are generally organic compounds containing nitro, azide and hydrazino groups. These materials produce energy by oxidation with a sudden release of energy when they undergo decomposition.[2]

It is well known that the use of high energy materials in their pure form is very rare; most energetic materials (*e.g.* RDX, HMX and CL-20) are used in conjunction with inert materials (*e.g.* HTPB and DOA) as well as other energetic materials (*e.g.* GAP and PLN) in high explosive and propellant formulations. One of the major ingredients of propellants and explosives is a polymeric binder that generally requires a small quantity of plasticizer to enable processing. Currently, hydroxy-terminated polybutadiene (HTPB) is in use and has excellent elastomeric properties. However, it contains little energy and requires a high solid loading, *i.e.* percentage of filler, to exhibit a good performance.[3] The use of such conventional polymers for explosive and propellant formulations brings down the overall energy of such systems.[4] Moreover, due to the sensitive nature of the 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 an energetic binder, which enables lowering of the solid loading or maintenance of the same solid loading with an enhanced performance.[5,6] This is the genesis of the energetic binder. The use of an energetic binder, *e.g.* GAP (poly-glycidyl azide), allows for a lower solid loading but results in dissatisfactory mechanical properties such as tensile strength, % elongation, initial modulus and hardness.[7] The polar groups in the molecular structures of these compounds increase their viscosity and elevate their glass transition temperatures. The increase in glass transition temperature downgrades the low-temperature characteristics, which is especially important for missile propellants. Designing 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 necessary modifications of the weapon system, the explosive formulation or a combination of both. One of the most successful methods is the use of insensitive energetic binder ingredients, wherein the explosive components are bound together by a polymeric binder, forming a rubbery material that is less susceptible to shock and other stimuli.[8] Poly-glycidyl nitrate (PGN) has emerged as a promising energetic binder for insensitive munitions and is worth investigating.[4,7] Since the performance of any energetic binder mainly depends on its ability to contain solid ingredients such as crystalline explosives, a solid loading of more than 80% is always preferable for the development of various munitions. In order to achieve this in the case of PGN, it is recommended that PGN is combined with a suitable plasticizer. Various types of plasticizers can be used for this purpose but choosing a suitable or compatible plasticizer can be difficult as the processing needs to be considered as well as the end use of the material. A plasticizer is usually defined in terms of the desired properties of a given polymer/plasticizer system.[9] A 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 optimally energetic plasticizers, which have a low glass transition temperature, a low viscosity, a low ability to migrate, a high oxygen balance and are also thermally stable.[10]

Compatibility testing of the ingredients of explosives and propellants is carried out to ensure safety during storage and reliability in service by determining whether their properties are adversely affected by any of the materials that are used near or are 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 required solid loading capacity. Therefore, energetic components are preferred. Hitherto, the known energetic plasticizers have disadvantages 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 stabilizers; however, finding a molecule that is stable as such is a very interesting area of research. Nitrate esters are important plasticizers in nitrate ester plasticized polyether (NEPE) propellants and other double-based propellants. Incorporating a nitrate ester plasticizer into propellant formulations can improve their mechanical properties at low temperatures and make them safe to use.[12–15] Experimental studies using thermal and rheological[16,17] techniques as well as computational studies at a molecular level[18] may be useful in understanding the compatibility of

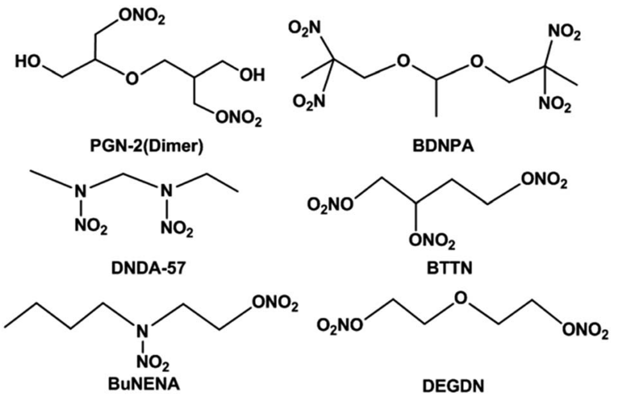


Chart 1 Molecular structures of energetic binder poly-glycidyl nitrate (dimeric form) and energetic plasticizers.

a PGN binder with different plasticizers (Chart 1), which include nitrate esters as well as the nitramine class, and also to gain a better insight with respect to the selection of a suitable plasticizer. Therefore, the present paper deals with the rheological behavior of PGN blended with different types of energetic plasticizers in terms of shear viscosity in order to make processable compositions with better solid loading.

2 Methodology

2.1 Experimental

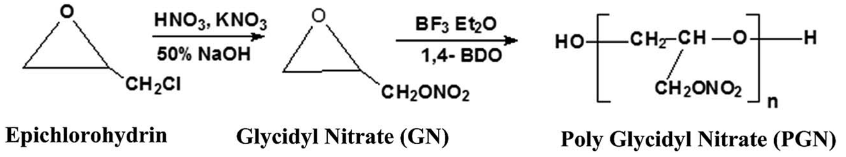
For the synthesis of PGN, reactants such as epichlorohydrin (Loba Chemie), sodium hydroxide (Ranbaxy, AR), nitric acid (Rankem, 70%), 1,4-butane diol (99% Fluka), BF_3 etherate (48%, Fluka), sodium chloride (Rankem), sodium sulphate (anhydrous, Rankem), sodium bicarbonate (Ranbaxy, AR), potassium nitrate (Qualigens, AR) and dichloromethane (Rankem) were used as received from the manufacturer without further purification. The structure of the intermediates, the monomer and the final polymers were studied using ^{1}H NMR spectra obtained on a Bruker-300 MHz instrument using tetra methyl silane (TMS) as an internal reference and $CDCl_3$ as the solvent. IR spectra were obtained on a Perkin Elmer FT-IR 1605 spectrophotometer using a smear method. UV-Vis spectra were obtained on a GBC Cintra 10e UV-Vis spectrophotometer using acetonitrile as solvent (concentration 1 mg ml^{-1}). The purity of the compound was determined by high performance liquid chromatography (HPLC) (Dionex Ultimate 3000) at a flow rate of 1 ml min^{-1}. 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 a 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-bottomed flask fitted with a condenser, a stirrer and a dropping funnel, nitric acid (50 ml, 60%) and potassium nitrate (30.3 g, 0.3 mol) were added. The reaction temperature of the contents was maintained at 10 °C and epichlorohydrin (92.5 g, 1 mol) was added dropwise over a period of 3 h keeping the temperature in the range 8–12 °C. To the abovementioned reaction mixture, 50% aqueous sodium hydroxide (112 g) was added at 5 °C over a period of 3 h and the mixture was left overnight at room temperature. The organic layer was extracted with dichloromethane (50 ml × 2) and washed with water (100 ml × 2). It was then dried over anhydrous sodium sulphate (20 g) and dichloromethane (100 ml) was removed under vacuum. The obtained GN was purified by distilling at 45 °C under reduced pressure (5 mm Hg). Yield: (36 g, 30%).

(b) Synthesis of poly-glycidyl nitrate (PGN). Dichloromethane (10 ml) was placed in a 250 ml three-necked round-bottomed flask, to which BF_3 etherate (3.55 g, 0.025 mol) and 1,4-butane diol (BDO) (1.12 g, 0.0125 mol) were added at 20 °C and stirred for 30 min in a nitrogen atmosphere. Glycidyl nitrate (59.5 g, 0.5 mol) in 40 ml dichloromethane was then added to the abovementioned solution dropwise over 3 h, maintaining the temperature at 13 ± 2 °C. The reaction mixture was stirred at room temperature for 24 h. The polymerization reaction was terminated with a brine solution and the polymer was extracted with dichloromethane. It was washed with aqueous sodium bicarbonate solution and water, and the dichloromethane (DCM) solvent containing PGN was dried over anhydrous sodium sulphate. The polymer (PGN) was precipitated by adding cold methanol (~10 °C) to the DCM solution and dried under vacuum at 50 °C. Yield: (47.5 g, 80%).

All the characterization data for GN and PGN have been appended in the ESI.† Similarly, synthetic procedures for the plasticizers along with the reaction schemes and the characterization data have been provided in the ESI.†

When using DSC as a technique for determining the compatibility, the results obtained for the pure product with respect to decomposition temperature and glass transition temperature are compared with the results obtained for the binder/plasticizer mixtures. If the peak related to a mixture moves to a temperature lower than the peak related to an energetic material or the material under test, this indicates incompatibility. The degree of incompatibility is measured by the difference in temperature between the peaks. PGN was synthesized in two steps, namely, the synthesis of the 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 the laboratory using reported methods. Other chemicals and reagents used in this study were used as received from the manufacturer. All the energetic plasticizers (20% w/w) were hand-mixed with PGN (80% w/w) and kept for 24 h at room temperature. After 24 h, these blends were observed for phase separation and then used for further studies as discussed in the results and discussion section. DSC samples (weight between 5 and 10 mg) were sealed in an aluminium pan. Thermal decomposition and glass transition temperatures of all the polymer blends were determined using a Perkin Elmer DSC (DSC-7) in the temperature range from −60 °C to 400 °C with a constant heating rate of 10 °C min^{-1} under a nitrogen



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

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 a 20 mm diameter parallel plate (20 ETC) at a gap of 0.5 mm. The steady shear data were collected from a shear rate sweep from 1 to 100 s^{-1}. All experiments were carried out at a constant temperature of 30 °C. A pre-shear period of 30 seconds was used to standardize the handling of samples before the measurement.

2.2 Computational

For the computational studies, all the geometries were fully optimized by employing the popular Becke three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang and Parr (B3LYP),[27,28] in conjunction with the 6-311(d,p) basis set. Such methods have already been employed in other works wherein intermolecular interactions play a 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 of theory to generate Molecular Electrostatic Potential (MESP) surfaces in the gas phase. All quantum chemical calculations were performed using the Gaussian 09, Revision C.01 program.[32] MESP surfaces have been generated with the Gauss View 5.0 suit of programs. The interaction energy ($\Delta E_i^{\ddagger}$) 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 eqn (1) wherein Z_A is the charge on nucleus A located at R_A and $\rho(r')$ is the electron density.[34]

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

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

3 Results and discussion

3.1 Thermal studies

Differential scanning calorimetry (DSC) was performed to compare the decomposition patterns of binder entities with and without plasticizer. In order to study the plasticizing effect of given plasticizers on a PGN binder through thermal studies, DSC analysis was carried out in terms of the glass transition temperature (T_g) and the thermal decomposition temperature ($T_{\max}$) of the binder and of binary mixtures of binder/plasticizer. The properties of the PGN binder are given in Table 1. The 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^{-1} as revealed by DSC.[44] To study the compatibility of energetic plasticizers with the energetic binder, PGN, all the plasticizers under consideration were thoroughly mixed with the binder. The plasticizer content in propellants can be varied from 0 to 35 wt% of the pure polymer. However, we considered a binder/plasticizer mixture at a ratio of 80 : 20 (w/w), as suggested in the literature.[45–47] After thorough mixing of 20% of various energetic plasticizers with the PGN (80%) binder, the resultant mixtures were kept at room temperature for 24 h or more to observe any phase separation. No layer separation or any other sign of heterogeneity has been observed, indicating the physical compatibility of the energetic plasticizers studied with the PGN binder. The decomposition peak profiles of the DSC analysis are shown in Fig. 1 and the corresponding peak temperatures ($T_{\max}$) are summarized in Table 2.

Table 1 Properties of poly-glycidyl nitrate (PGN)

S. no.	Properties	PGN
1	$\bar{M}_n$	2484
2	Viscosity (cPs)	5174
3	T_g (°C)	−34.95
4	ΔH_f (J g^{-1})	−2859
5	$T_{\max}$ (°C)	214

The DSC curve of PGN shows the main decomposition process in the temperature range 195–225 °C with only one exothermic peak at 214 °C, where the gaseous products are formed. From the DSC profile, (Table 2) it is found that the decomposition temperature ($T_{\max}$), *i.e.* 214 °C, is not significantly altered by the addition of 20% of energetic plasticizer in all the cases. Therefore, the characteristic decomposition temperatures remained practically unchanged when the plasticizer was added. Consequently, all the plasticizers can be considered to be compatible with PGN wherein safety is concerned. The decomposition energy of PGN generally decreases with the addition of plasticizers. However, in the case of BDNPA, an 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–NO_2 bond and result in lower decomposition temperatures for 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 explosives and contact materials are listed in Table 3.[49,50] The decomposition of PGN is almost consistent during the addition of plasticizers with the minimal exothermic peak variation in the range from 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 a deviation of ≤2 °C from the decomposition temperature ($T_{\max}$) (Table 2). DSC curves of such binary systems suggest that there is an acceptable effect on the decomposition process of the binders and mixtures of binder/plasticizer. Therefore, the lack of new peaks, no alteration in

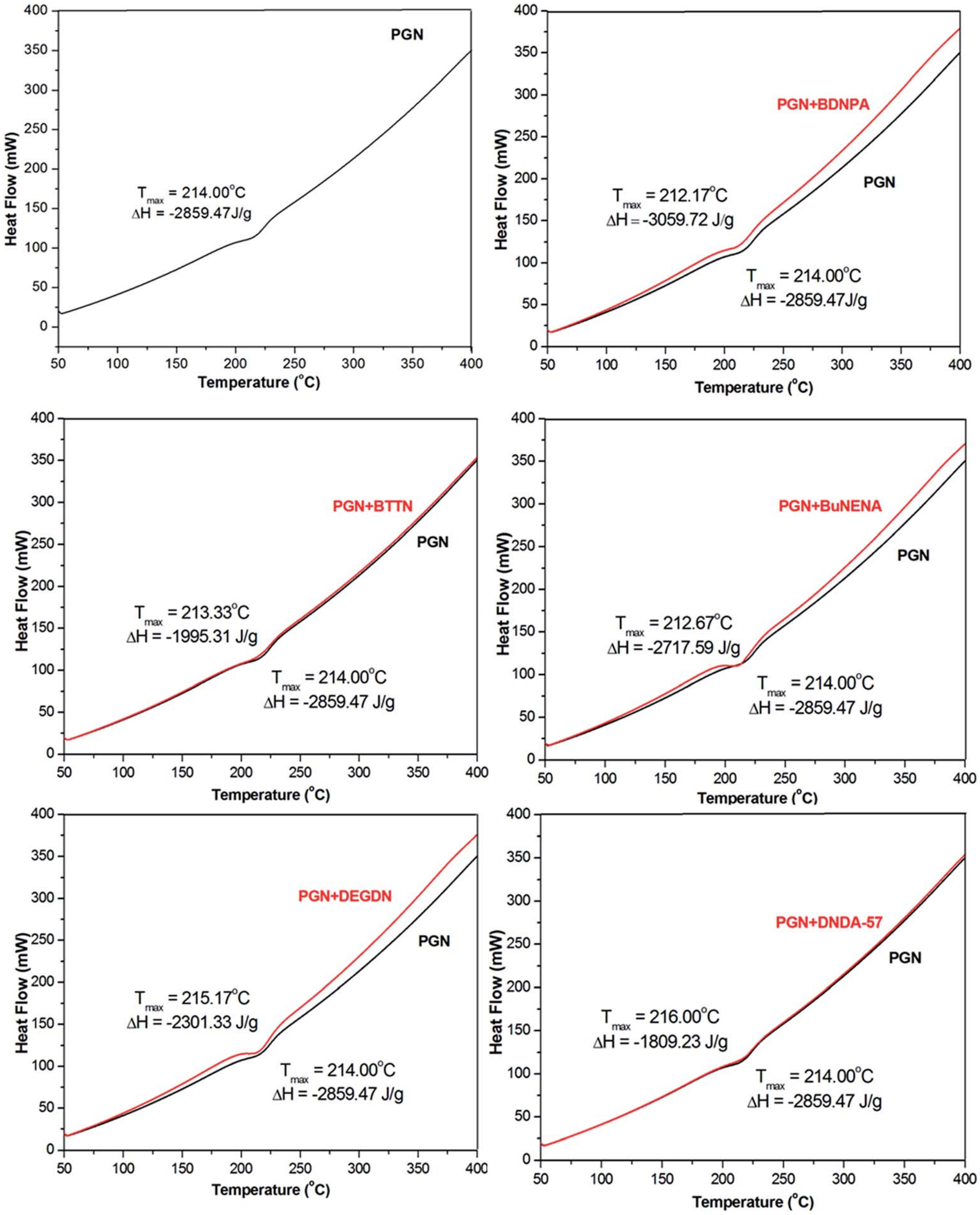


Fig. 1 DSC curves (heat flow endo up *vs.* temperature) of pure PGN and PGN mixed with different plasticizers.

Table 2 Effect of addition of different plasticizers on glass transition temperature (T_g) and decomposition temperature (T_{max})

S. no.	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

the peak format and the similar decomposition peak temperatures, with and without plasticizer, indicate the compatibility of PGN with the energetic plasticizers studied.

The glass transition occurs when the movement of molecules in the system is restricted due to the low temperature at which the binder changes from rubbery to brittle. The phenomenon of plasticization results from the addition of a diluent (called a *plasticizer*) to a polymer, with which it is miscible in all proportions so as to lower the resultant glass transition temperature (T_g). Considerable data have been produced regarding the effect of the monomer mixture on the T_gs of copolymer systems.[51–56] The T_g of a number of polymer and plasticizer mixtures at various polymer-to-plasticizer ratios was determined. The molecular flexibility of the plasticizer is an important factor in 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. Herein, all the plasticizers were used to reduce the T_g of PGN

Table 3 Evaluated standards of compatibility for explosives and contact materials

S. no.	Deviation from T_{max}	Rating	Description
1	≤ 2	A	Safe for use in any explosive formulation
2	3–5	B	Safe for testing purposes over a short period of time
3	6–15	C	Not recommended for use with explosive items
4	>15	D	Hazardous. Should not be used under any conditions

and to increase the processability of the binder/plasticizer blend. The effect of plasticizer addition was observed in terms of lowering of the T_g of PGN, which again indicates the compatibility of plasticizers with PGN. The maximum lowering of T_g (−53.01 °C) is found in the case of BuNENA (Fig. 2), while BDNPA, DNDA-57 and DEGDN give T_g at −44.91 °C, −51.20 °C and −45.24 °C, respectively, BTTN has shown the minimum lowering of the T_g at −39.38 °C. The single point T_g values for all the combinations is evidence of the presence of a single-phase homogeneous system, which confirms the thermodynamic compatibility of the energetic binder with energetic plasticizers.[45,55,56] All these PGN/plasticizer blends showed reduced glass transition temperatures as observed by low-temperature DSC, which also confirms the compatibility of the PGN binder with the plasticizers. This is due to a reduction in the cohesive forces of attraction between polymer chains as the plasticizer introduces free volume in the material and like any solvent, promotes polymer–plasticizer interactions at the expense of polymer–polymer interactions.[52–54] The possibility of low barriers for segmental motion of the polymer backbone when plasticizers are added to the 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 a reduction in the glass transition temperature (T_g) of the blend. Therefore, BuNENA/PGN and DEGDN/PGN blends show a maximum lowering of T_g due to the presence of weak interactions with the polymer backbone compared to all the other plasticizer/binder blends.

Based on these desirable characteristics of BuNENA/PGN and DEGDN/PGN blends, it is proposed that BuNENA and DEGDN seem to be the most suitable plasticizers for PGN in order to achieve the maximum solid loading and better processing. However, the ability to lower 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 the energetic binder, PGN. The development of a theory for the prediction of composition-dependent glass-transition temperatures for multi-component mixtures, which manifests single glass transitions, is of fundamental interest and moreover, has practical merit in connection with their processing conditions and in-service properties.

3.2 Rheological studies

Compatibility of a polymeric binder with a plasticizer is possible when they mix to form a 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 the energetic binder, PGN, with all the five plasticizers, the samples prepared for the abovementioned thermal studies were also subjected to rheological studies.[58] The ability of the plasticizers to lower the viscosity of the polymer was measured for 80 : 20 mixtures of PGN and plasticizer as in the thermal studies. In order to study the flow behavior in terms of viscosity of PGN and PGN/plasticizer blends, a shear rate sweep (Fig. 3) from 1 to 100 s^{-1} was performed at a 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 is too high to be considered for solid loadings of more than 50% (w/w). After addition of 20% (w/w) energetic plasticizers, it has been observed that the viscosity of the binder/plasticizer blend has reduced drastically, along with an increase in the flow behavior. Although the quantity of the plasticizer added to the binder is fixed, the mixes showed different flow behavior with respect to viscosity. The addition of DEGDN imparts the maximum effect in reducing the viscosity up to 897 cPs from 5174 cPs, (Fig. 3). A similar effect is observed with other plasticizers but not 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 the polymer is the major component in a typical polymer/plasticizer system; it is possible to use the viscosity of dilute polymer solutions as a 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 with poor solvent power causes the segments of the polymer chain to stay close to each other, leading them 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 and flow, which in turn leads to 'softening' or 'plasticization' of the polymeric material. The abovementioned behavior of any plasticizer depends on the polarity, size (molecular weight) and shape (linear/branching) of plasticizer molecules. Therefore, different plasticizers behave differently in a given polymer. DNDA-57 is a nitramine plasticizer and it contains two $-NNO_2$ groups, whereas there are four $-CNO_2$ groups in the chemical structure of BDNPA as it belongs to the nitro class of plasticizers. Similarly, DEGDN and BTTN belong to the nitrato class of plasticizers since they contain two and

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DOI: 10.1039/C5RA16476A

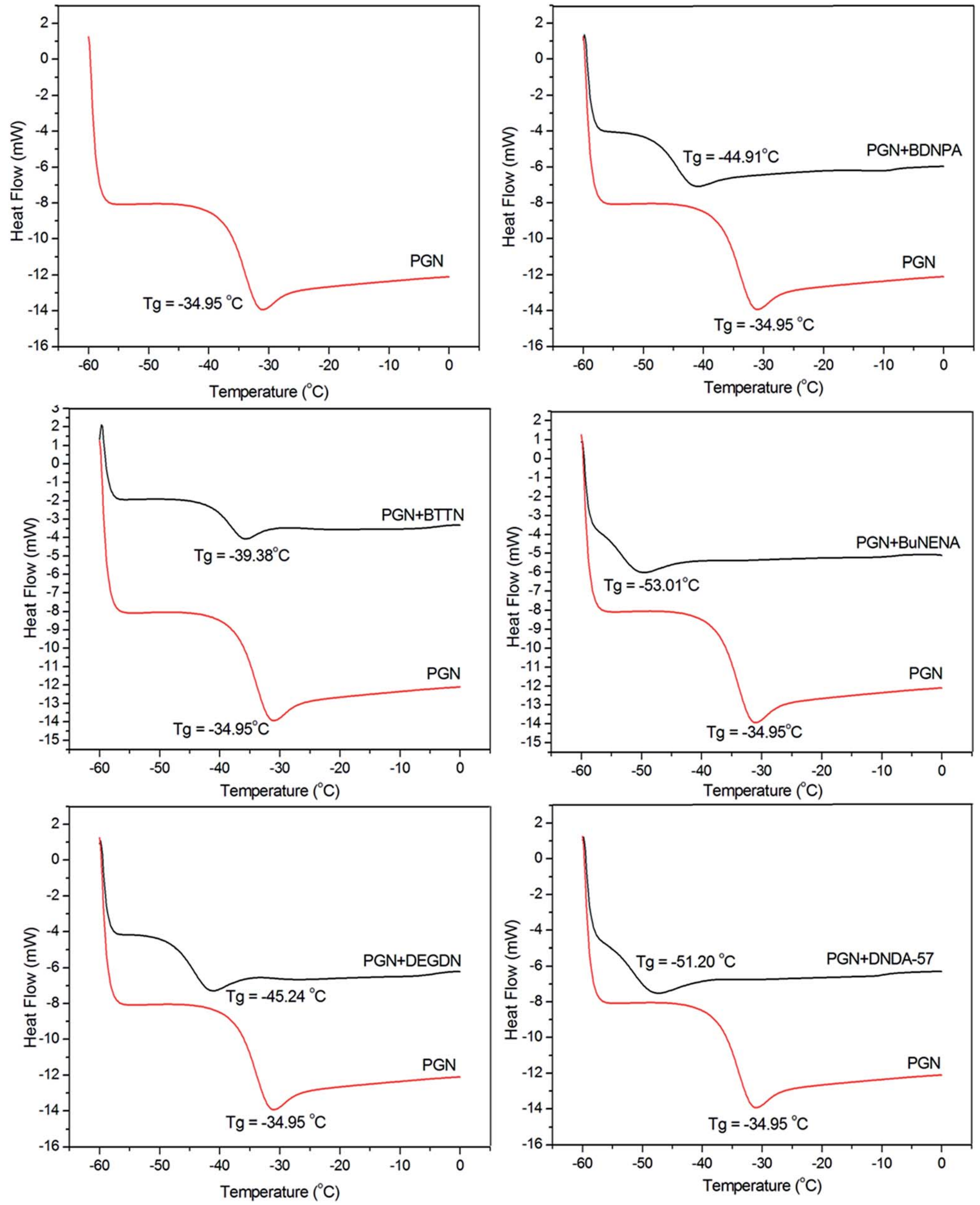


Fig. 2 Low-temperature DSC curves of pure PGN and PGN mixed with different plasticizers.

three $-ONO_2$ groups, respectively. BuNENA belongs to the nitrato-nitramine class as it contains both $-ONO_2$ and $-NNO_2$ groups. Consequently, the relative ability of plasticizers towards reducing the viscous nature of the resultant mixture (binder/plasticizer) may be anticipated to be in the order BDNPA < DNDA-57 < BuNENA < BTTN < DEGDN. Therefore, DEGDN ranks highest in reducing the viscosity because it causes loose binding interactions between segments of the polymeric binder, PGN.

3.3 DFT studies

To obtain the maximum benefit with respect to mechanical properties from this polymer system, the polymeric networks must be physically compatible with the energetic plasticizer molecules. Therefore, an understanding of the interactions between polymer and plasticizer is essential. In order to understand the compatibility of the energetic polymeric binder, PGN, with different energetic plasticizer molecules and the factors responsible for the resultant flow behavior of binder/plasticizer mixtures, we attempted quantum chemical calculations employing DFT methods at the B3LYP/6-311G(d,p) level of theory. As in the experimental study, we 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 optimized the plasticizer molecules at the B3LYP/6-311G(d,p) level to obtain stable conformers. To minimize the computational effort for the electronic structure calculations, model compounds whose structures resembled the terminal

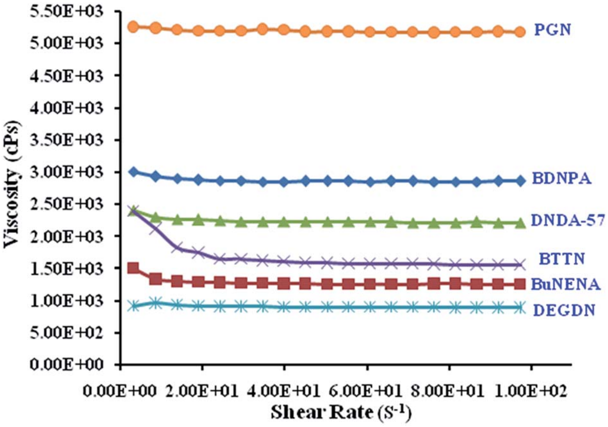


Fig. 3 Shear rate sweep test of PGN and PGN mixed with different plasticizers (20% w/w).

branches of actual compounds were considered for two molecules. They are (1) the polymeric binder, PGN, which is modeled with its dimeric form and (2) the DNDA-57 plasticizer as a mixture of three homologous 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 considered DNDA-6 in our computational study since it may be the best simulant of DNDA-57 for studying the compatibility of DNDA-57 with PGN as it contains both methyl and ethyl groups at its terminal positions. Henceforth, we will refer to 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 intermolecular interaction studies.

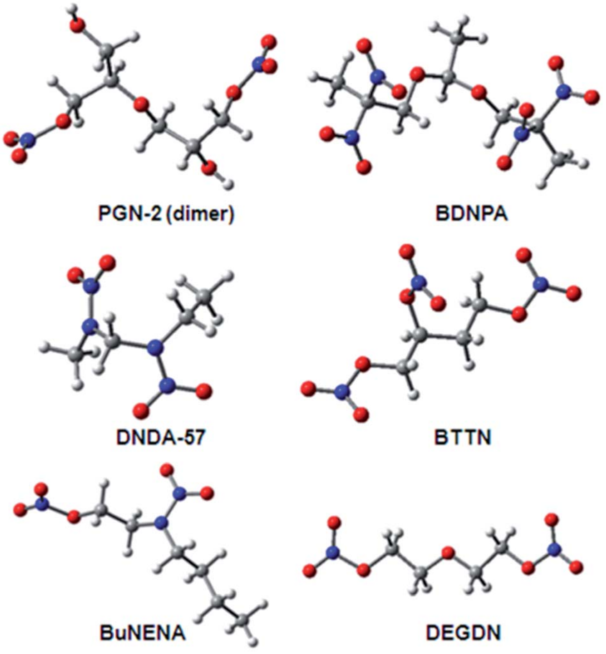
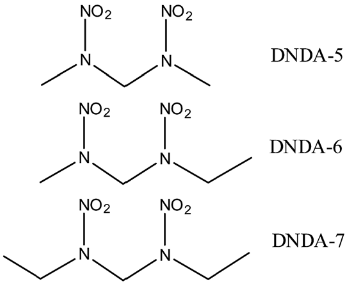


Chart 2 Optimized geometries of PGN-2 (dimer) and energetic plasticizers at the B3LYP/6-311G(d,p) level of theory (grey: carbon; red: oxygen; blue: nitrogen; white: hydrogen).

Initially, we generated the MESP surfaces for the dimeric PGN binder and the five plasticizer molecules to identify possible sites of interactions between them. MESP is an important tool and has been a widely used topographical quantity for understanding molecular reactivity, making coarse guesses about intermolecular interactions, molecular recognition, electrophilic reactions and substituent effects.[35–43] MESP analysis gives the most negative potential point ($V_{\min}$) in the electron-rich regions obtained through topography calculations in any molecular system (Fig. 4). It is obvious that the plasticizers will show possible locations of $V_{\min}$ near respective explosophores (–NNO_2/–CNO_2/–ONO_2). From Table 4, it is clear that the $V_{\min}$ of the nitro (–CNO_2) group is more negative than that of the nitrato (–ONO_2) group. It is also clear that the $V_{\min}$ of the nitramine (–NNO_2) group is even more negative than that of the nitro (–CNO_2) group. From this, it is deduced that plasticizers containing the nitramine group may have a higher reactive tendency towards PGN than plasticizers that contain nitro and nitrato groups. However, the binding ability of plasticizers further depends on the number of such explosophores. BDNPA and BTTN possess a greater number of interaction sites with four and three explosophores, respectively, than BuNENA, DNDA and DEGDN, which contain only two interaction sites 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 BDNPA > DNDA-57 > BuNENA > BTTN > DEGDN. It may be expected that the relative interactivity trend of the plasticizers will correspond to this total MESP $-$ $V_{\min}$ trend. In general, reduced viscosity in the resultant polymer matrix can occur as a result of weak or loose intermolecular interactions. Consequently, the relative ability of plasticizers towards reducing the viscous nature of the resultant mixture (binder/plasticizer) may be anticipated to be in the increasing order BDNPA < DNDA-57 < BuNENA < BTTN < DEGDN. Therefore, DEGDN ranks highest 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 solely on the basis of MESP $-$ $V_{\min}$ values when intermolecular interactions between binder and plasticizer also play



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

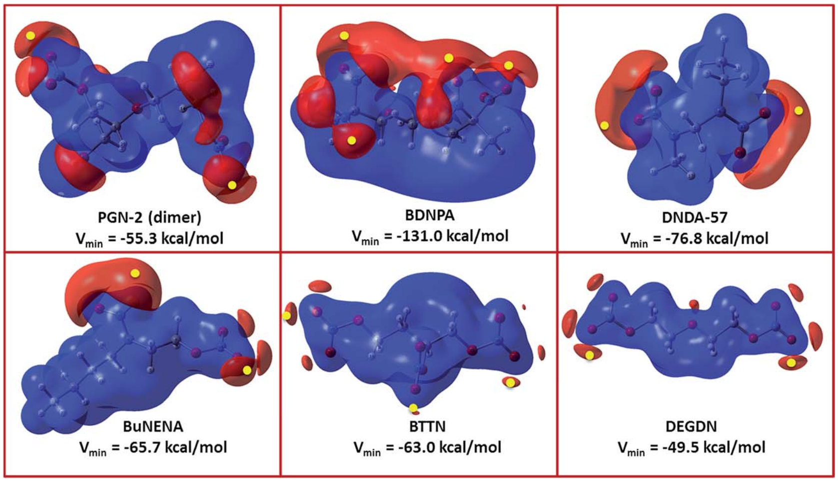


Fig. 4 MESP surfaces generated for PGN dimer and energetic plasticizers at the B3LYP/6-311G(d,p) level of theory along with the corresponding total V_{min} of explosophores. The yellow dot represents the location of the V_{min} point in each explosophore (red: electron rich regions; blue: electropositive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

a role. Therefore, we considered the binder and plasticizers in this study, involving intermolecular interactions in order to understand the compatibility of plasticizers with binders.

Initially, we carried out studies on the interactions of plasticizers with one segment of PGN-2 (details are provided in ESI†). Moreover, the interactions of plasticizers 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 plasticizers as models of binder/plasticizer systems are presented in Fig. 5 along with the resultant intermolecular interactions indicated with dotted lines. In all cases, optimizations of various starting geometries converge to different interaction types, in which the plasticizer molecule is oriented by the NO_2 group or by the C–H groups in between two binder fragments. The computed intermolecular distances and free energies reveal that the molecular C–H groups play the main role in the interactions of plasticizers, which are mainly oriented by the C–H groups towards two segments of PGN-2. In this study, the two fragments of PGN-2 form a complex with BDNPA through three –C–H⋯O– interactions (2.467 Å, 2.545 Å and 2.494 Å) and two –O–H⋯O hydrogen bonding interactions at distances of 2.044 Å and 2.086 Å. A complex of two molecules of PGN-2 with BTTN involves two –C–H⋯O– interactions (2.616 Å and 2.507 Å) and two –O–H⋯O (2.118 Å and 2.145 Å) hydrogen bonding interactions. A complex of PGN-2 and BuNENA consists of two H-bonds (2.175 Å and 2.001 Å) and two weak –C–H⋯O– interactions (2.527 Å and 2.562 Å). Similarly, the distances 2.580 Å, 2.326 Å, 2.348 Å and 2.524 Å correspond to –C–H⋯O– interactions, whereas the distances 2.010 Å and 2.012 Å correspond to –O–H⋯O H-bonding interactions 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 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 complexes 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^{-1}, Table 5). The computed interaction energy results in terms of electronic and Gibbs free energies suggest that BDNPA interacts more strongly with PGN-2, whereas DEGDN has the lowest interaction compared to all the other plasticizers (Table 5). The computed results show that the interaction trend of plasticizers varies for DNDA-57 and BTTN in the study of a single fragment (PGN2-plasticizer) compared to the theoretical MESP trend and the experimental viscosity trend. However, the computed interaction energy trend of adducts of PGN2–plasticizer–PGN2 was found to be well matched with the V_{min} trend of the MESP analysis and the experimental viscosity trend. Therefore, the interaction ability of plasticizers predicted using two segments of PGN-2 may be more accurate as it mimics the introduction of plasticizer between the polymeric segments of the binder. It would be even

Table 4 All possible V_{min} values (kcal mol^{-1}) for plasticizers available for interaction with binder

S. no.	Molecule	V_{min} (–NNO_2)	V_{min} (–CNO_2)	V_{min} (–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

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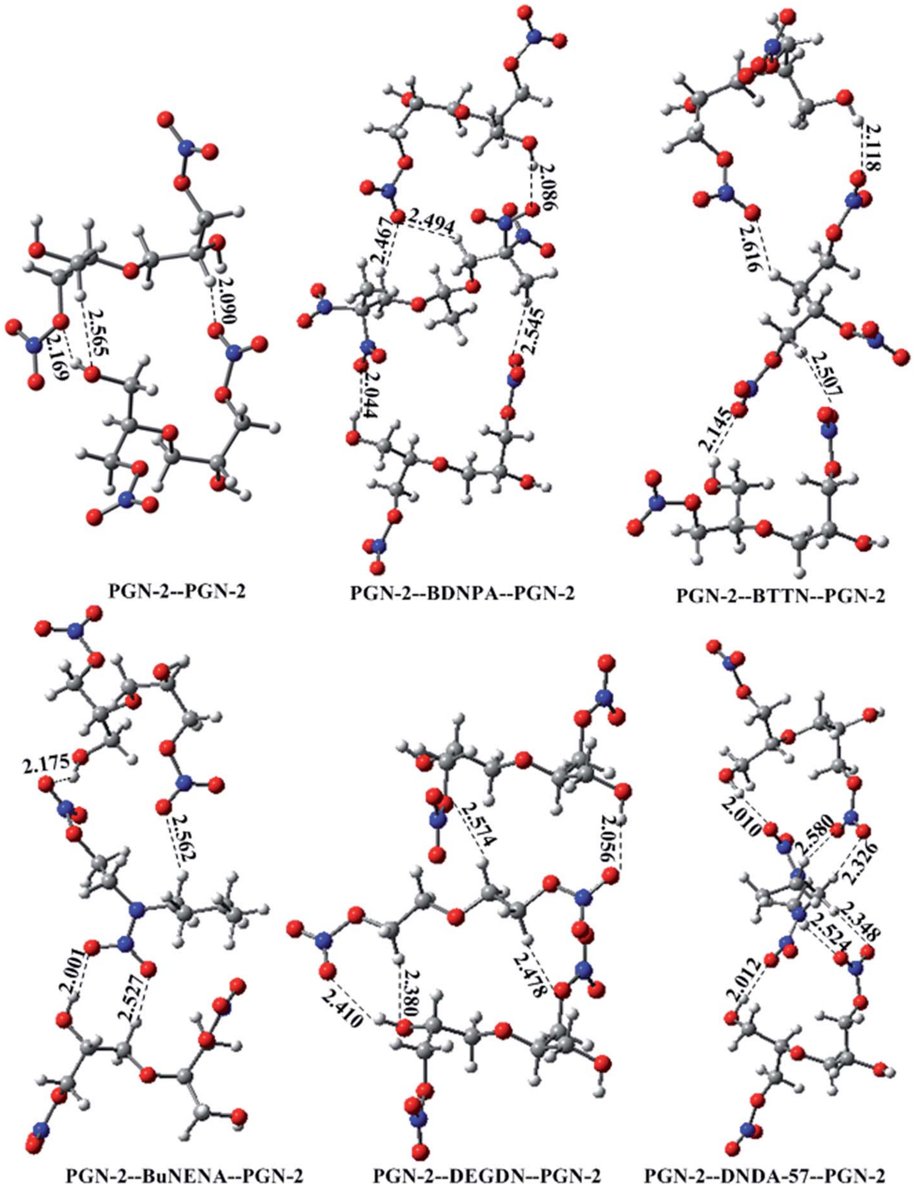

PGN-2--PGN-2 PGN-2--BDNPA--PGN-2 PGN-2--BTTN--PGN-2

PGN-2--BuNENA--PGN-2 PGN-2--DEGDN--PGN-2 PGN-2--DNDA-57--PGN-2

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

more realistic if one could consider a higher number of polymer segments. However, we restricted our modeling studies to two polymeric segments to avoid increasing the number of atoms, which is expensive due to the computational power required.

In general, 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

Table 5 Electronic and Gibbs free energies (kcal mol^{-1}) for interactions between plasticizers and binder (PGN-2)

		Electronic energies		Gibbs free energies	
S. no.	Plasticizer	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

between polymer/plasticizer blends. Polymers such as PGN, containing nitrato (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, causing –C–H⋯O– interactions with the plasticizer. In practice, the plasticization effect often involves specific interactions or the formation of excess volume upon mixing the polymer and plasticizer, which lead to negative T_g deviations. As per the interaction energies reported in Table 5, the plasticizers BuNENA and DEGDN cause weak interactions (due to having fewer functional groups) with the polymer backbone compared to other plasticizers, which correlates well with the fact that these plasticizers showed a maximum reduction in the glass transition temperature in experimental thermal studies, as mentioned in Section 3.1.

4 Conclusions

The compatibility of PGN with energetic materials in propellants or explosives is the most important aspect of PGN in practical applications. However, investigations on this aspect are rarely reported. Therefore, this study investigates the interactions and compatibilities between PGN and some common energetic plasticizers. The effects of the addition of five different energetic plasticizers *viz.* BDNPA, DNDA-57, BuNENA, BTTN and DEGDN to 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 the 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 it to a minimum extent (−39.4 °C). Similarly, a maximum increase in flow behavior (lowering of viscosity) has been observed by the addition of DEGDN, whereas a minimum increase in flow behavior resulted from the addition of BDNPA. The relative ability of plasticizers towards reducing the viscosity of the resultant plasticizer/binder blend is in the increasing order BDNPA < DNDA-57 < BuNENA < BTTN < DEGDN. This has been explained on the basis of intermolecular interactions employing density functional calculations using Gibbs free energies and electronic energies of interaction. All the five plasticizers BuNENA, DEGDN, BDNPA, BTTN and DNDA-57 were found to be suitable/compatible for the energetic binder, PGN. Moreover, it has been observed that DEGDN and BuNENA showed the highest compatibility with PGN.

Acknowledgements

The authors are grateful to R. Vijayalakshmi for providing the DNDA-57 sample for thermal and rheological studies. The authors also thank Dr Sudheer, ACRHEM, University of Hyderabad and Ms Suman Pawar for extending their support in thermal studies. We sincerely acknowledge the Bioinformatics Resources and Application Facility (BRAF) at the Center for Development of Advanced Computing (C-DAC), Pune for benevolently permitting the remote access of high performance computational power. We also thank the anonymous reviewers for their comments and suggestions that have helped us to improve the paper.

References

1 J. P. Agrawal, *High Energy Materials: Propellants, Explosives and Pyrotechnics*, WILEY-VCH Verlag GmbH & Co. KGaA, 2010, pp. 9–81.
2 D. M. Badgujar, M. B. Talawar, S. N. Asthana and P. P. Mahulikar, *J. Hazard. Mater.*, 2008, **151**, 289–305.
3 A. Provatas, DSTO-TR-0966, Aeronautical and Maritime Research Laboratory (AMRL)-DSTO, 2000.
4 E. Diaz, P. Brousseau, G. Ampleman and R. E. Prud'homme, *Propellants, Explos., Pyrotech.*, 2003, **28**, 101–106.
5 J. P. Agrawal, *Prog. Energy Combust. Sci.*, 1998, **24**, 1–30.
6 K. Selim, S. Ozkar and L. Yilmaz, *J. Appl. Polym. Sci.*, 2000, **77**, 538–546.
7 R. L. Willer, *J. Mex. Chem. Soc.*, 2009, **53**, 108–119.
8 J. Kaur, V. P. Arya, G. Kaur and P. Lata, *Cent. Eur. J. Energ. Mater.*, 2013, **10**, 371–391.
9 R. S. Damse and A. Singh, *Def. Sci. J.*, 2008, **58**, 86–93.
10 W. Niklas and E. Carina, *Propellants, Explos., Pyrotech.*, 2002, **27**, 314–319.
11 N. E. Beach and V. K. Canfield, Compatibility of explosives with polymers (III), *PLASTEC Rep.*, 1971, 40–73, AD 721004.
12 Y. P. Ji, P. R. Li, W. Wang, Y. Lan and F. Ding, *Chin. J. Explos. Propellants*, 2005, **4**, 47–50.
13 X. B. Zhao, X. P. Zhang, J. Zheng and L. Du, *J. Solid Rocket Technol.*, 2001, **24**, 31–34.
14 Z. G. Feng, *Chem. Propellants Polym. Mater.*, 1999, **70**, 1–10.
15 Y. Liui, L. Wang, X. Tuo, S. Li and W. Yang, *J. Serb. Chem. Soc.*, 2010, **75**, 987–996.
16 S. Honary, H. Orafai and A. Shojaci, *Drug Dev. Ind. Pharm.*, 2000, **26**, 1019–1024.
17 G. B. Thurston and A. Martin, *J. Pharm. Sci.*, 1978, **68**, 678–689.
18 X. Jijun, H. Hui, Li. Jinshan, Z. Hang, Z. Wei and X. Heming, *J. Mol. Struct.: THEOCHEM*, 2008, **851**, 242–248.
19 R. L. Willer, R. S. Day and A. G. Stern, Process of producing improved poly(glycidyl nitrate), US Patent 5,120,827, Application No. 561,797, June 9, 1992, Date of filing: 02 August 1990.
20 R. L. Willer, R. S. Day and A. G. Stern, Process of producing improved poly(glycidyl nitrate), E. Patent 0,471,489 B1, Application No. 91307155.1, February 19, 1992, Date of filing: 02 August 1991.
21 G. M. Gore, R. G. Bhatewara, K. R. Tipare, N. M. Walunj and V. K. Bhat, *Int. Annu. Conf. ICT*, 1998, **29**, 136.
22 R. S. Hamilton and R. B. Wardle, Synthesis of bis(2,2-dinitropropyl)acetal (BDNPA), US Patent 5,648,556, Application No. 339,138, July 15, 1997, Date of filing: 14 November 1994.
23 T. Knott, Method for producing dinitro-diaza-alkanes and interediate products thereto, US Patent 0,041,936 A1,

View Article Online
DOI: 10.1039/C5RA16476A

Application No. 09/959,631, March 6, 2003, Date of filing: 02 March 2001.

24 N. A. Straesslere, A. J. Paraskos and M. P. Kramer, Methods of producing nitrate esters, US Patent 8,658,818, B2, Application No. 12/953,111, February 25, 2014, Date of filing: 23 November 2010.

25 N. A. Straesslere, A. J. Paraskos and M. P. Kramer, Methods of producing nitrate esters, US Patent 0,130,115 A1, Application No. 12/953,111, May 24, 2012, Date of filing: 23 November 2010.

26 K. P. C. Rao, A. K. Sikder, M. A. Kulkarni, M. M. Bhalerao and B. R. Gandhe, *Propellants, Explos., Pyrotech.*, 2004, **29**, 93–98.

27 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

28 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.

29 M. A. S. Khan, R. Lo, T. Bandyopadhyay and B. Ganguly, *J. Mol. Graphics Modell.*, 2011, **29**, 1039–1046.

30 M. A. S. Khan and B. Ganguly, *J. Mol. Model.*, 2012, **18**, 1801–1808.

31 M. A. S. Khan, T. Bandyopadhyay and B. Ganguly, *J. Mol. Graphics Modell.*, 2012, **34**, 10–17.

32 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford, CT, 2010.

33 M. A. S. Khan, A. Sen and B. Ganguly, *CrystEngComm*, 2009, **11**, 2660–2667.

34 *Reviews in Computational Chemistry*, ed. P. Politzer, J. S. Murray, K. B. Lipkowitz and D. B. Boyd, VCH Publishers, New York, 1991, vol. 2, ch. 7, pp. 273–312.

35 R. K. Pathak and S. R. Gadre, *J. Chem. Phys.*, 1990, **93**, 1770–1773.

36 E. Scrocco and J. Tomasi, *Adv. Quantum Chem.*, 1978, **11**, 116–193.

37 J. S. Murray and P. Politzer, *J. Mol. Struct.: THEOCHEM*, 1998, **425**, 107–114.

38 T. Brinck, J. S. Murray and P. Politzer, *Mol. Phys.*, 1992, **76**, 609–617.

39 M. A. S. Khan, J. Zhang, K. D. Sarma and B. Ganguly, *RSC Adv.*, 2012, **2**, 8460–8466.

40 G. Dive and D. Dehareng, *Int. J. Quantum Chem.*, 1993, **46**, 127–136.

41 P. Politzer and J. S. Murray, *J. Phys. Chem. A*, 1998, **102**, 1018–1020.

42 J. S. Murray, F. Abu-awwad and P. Politzer, *J. Phys. Chem. A*, 1999, **103**, 1853–1856.

43 M. A. S. Khan, A. Singh, S. Haldar and B. Ganguly, *Cryst. Growth Des.*, 2011, **11**, 1675–1682.

44 A. Provatas, DSTO-TR-1171 Aeronautical and Maritime Research Laboratory (AMRL)-DSTO, 2001.

45 D. Kumari, H. Singh, M. Patil, W. Thiel, C. S. Pant and S. Banerjee, *Thermochim. Acta*, 2013, **562**, 96–104.

46 V. Ramavat, N. H. Naik, G. M. Gore and A. K. Sikder, *J. Energ. Mater.*, 2015, **33**, 1–16.

47 K. Ghosh, J. Athar, S. Pawar, B. G. Polke and A. K. Sikder, *J. Energ. Mater.*, 2012, **30**, 107–123.

48 A. R. Merritt, R. Rajagopalan and N. J. Trivedi, *RSC Adv.*, 2012, **2**, 12298–12304.

49 J.-Z. Li, B.-Z. Wang, X.-Z. Fan, H.-J. Wei, X.-L. Fu, C. Zhou and H. Huo, *Def. Technol.*, 2013, **9**, 153–156.

50 W. P. C. de Klerk, M. A. Schrader and A. C. van der Steen, *J. Therm. Anal. Calorim.*, 1999, **56**, 1123–1131.

51 C. S. Pant, R. M. Wagh, J. K. Nair, G. M. Gore and S. Venugopalan, *Propellants, Explos., Pyrotech.*, 2006, **31**, 477–481.

52 D. Kumari, S. G. Anjitha, C. S. Pant, M. Patil, H. Singh and S. Banerjee, *RSC Adv.*, 2014, **4**, 39924–39933.

53 D. Kumari, R. Balakshe, S. Banerjee and H. Singh, *Review Journal of Chemistry*, 2012, **2**, 240–262.

54 H. G. Ang and S. Pisharath, *Energetic Polymers: Binders and Plasticizers for Enhancing Performance*, Wiley-VCH, 2012.

55 Q. Shaojun, F. Huiqing, G. Chao, Z. Xiaodong and G. Xiaoxian, *Propellants, Explos., Pyrotech.*, 2006, **31**, 205–208.

56 D. Drees, D. Loffel, A. Messmer and K. Schmid, *Propellants, Explos., Pyrotech.*, 1999, **24**, 159–162.

57 Y.-C. Lai, E. T. Quinn Jr and P. L. Valint, *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **33**, 1767–1779.

58 H.-X. Li, J.-Y. Wang and C.-W. An, *Cent. Eur. J. Energ. Mater.*, 2014, **11**, 237–255.