

2,2-Dinitro-1,3-Bis-Nitrooxy-Propane (NPN): A New Energetic Plasticizer

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Summary

A new energetic plasticizer, 2,2-dinitro-1,3-bis-nitrooxy-propane (NPN), has been characterized. Its high oxygen balance, +12.5%, and low glass transition temperature, -81.5°C (mid-point), makes it very attractive as an energetic plasticizer in solid propellants. The ability of NPN to lower the glass transition temperature and viscosity of uncured PolyNIMMO has been studied and compared to other energetic plasticizers, such as BDNPA/F and butyl-NENA. NPN has a similar plasticizing effect as butyl-NENA, both on depressing the glass transition temperature and lowering the viscosity. To increase the poor thermal stability of NPN, several conventional nitrocellulose/nitroglycerine stabilizers were evaluated. Further work is however needed to find a more effective stabilizer.

1 Introduction

By using energetic polymers, such as poly(3-nitratomethyl-3-methyl oxetane) (PolyNIMMO), it is possible to increase the specific impulse of a solid rocket propellant, compared to the current state of the art hydroxy-terminated polybutadiene (HTPB) propellants, by approximately 10%. PolyNIMMO has a glass transition temperature, T_g , at approximately -30°C and in general it increases by 10°C when cured⁽¹⁾. The glass transition temperature must be lower than the minimum service temperature (usually -40 to -55°C depending on the application), especially when the propellant is case-bonded, to avoid failure of the motor during firing. The glass transition temperature of PolyNIMMO can be depressed by using a suitable plasticizer. A plasticizer is also added to lower the viscosity of the uncured propellant to improve processing, since the solid loading, and thus the specific impulse, often is limited by processing ability.

To obtain a high specific impulse it is desirable to use energetic plasticizers. The optimum energetic plasticizer has a low glass transition temperature, a low viscosity, a low ability to migrate and a high oxygen balance. It should also be thermally stable and have a low impact sensitivity. These demands are in many cases contradictory and it is thus not easy to find the ultimate energetic plasticizer. Several energetic plasticizers, such as nitroethyl nitramines (NENAs)⁽²⁾, nitrate esters (e.g. nitroglycerine, butanetriol trini-

trate (BTTN) and trimethylolethane trinitrate (TMETN))⁽³⁾, azido compounds^(4,5), bis(2,2-dinitropropyl) acetal/bis(2,2-dinitropropyl)formal (BDNPA/F)⁽⁶⁾, nitroaromatic compounds (e.g. 2,4-/2,6-dinitroethylbenzene/2,4,6-trinitroethylbenzene (K10))⁽¹⁾ and nitrate oligomers (glycidyl nitrate and NIMMO oligomers)⁽⁷⁾, have been developed worldwide for use in solid propellants and plastic bonded explosives. 2,2-Dinitro-1,3-bis-nitrooxy-propane (NPN) has been proposed as a plasticizer for double base propellants, but no experimental data have been published⁽⁸⁾. This paper presents results from the characterization and evaluation of NPN as a potential energetic plasticizer in an energetic binder formulation.

2 Experimental

2.1 Materials

2.1.1 Polymer

- PolyNIMMO BX PP880, poly(3-nitratomethyl-3-methyl oxetane), 2-functional, (Nobel Enterprises, UK.)

2.1.2 Plasticizers

- Butyl-NENA, *N-n*-butyl-*N*-(2-nitroxy-ethyl)nitramine, (DYN0 Industrier ASA, Norway).
- BDNPA/F, bis(2,2-dinitropropyl)acetal/bis(2,2-dinitropropyl)formal (50/50), (Aerojet, USA).
- NPN, 2,2-dinitro-1,3-bis-nitrooxy-propane, (FOI, Sweden).

2.1.3 Stabilizers

- 2-NDPA, 2-nitrodiphenylamine, puriss (Fluka AG, Switzerland).
- Centralite I, 1,3-diethyl-1,3-diphenylurea (NEXPLO/Bofors, Sweden).
- NQ, nitroguanidine (Fluka AG, Switzerland).
- Akardite II, 1,1-diphenyl-3-methylurea (NEXPLO/Bofors, Sweden).
- DPA, diphenylamine, 98% (Merck, Germany).

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2.2 Methods

NPN was characterized by elemental analysis performed by H. Kolbe Mikroanalytisches Laboratorium, Germany.

The glass transition temperature, T_g , was measured using a Mettler DSC 30, differential scanning calorimeter, equipped with a ceramic sensor. Every test as well as the calibration was performed in a nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min. The samples were put in 40 µl aluminum cups with a pierced lid. The sample weight was between 10 and 20 mg. Calibration was made with indium (Mettler-Toledo, Sweden) ($T_m=156.6$ °C) and anhydrous *n*-octane (Sigma-Aldrich, Sweden) ($T_m=-57$ °C). All tests were performed in duplicate.

The density of NPN was measured at room temperature by using a precision syringe (50 µl) and a micro balance.

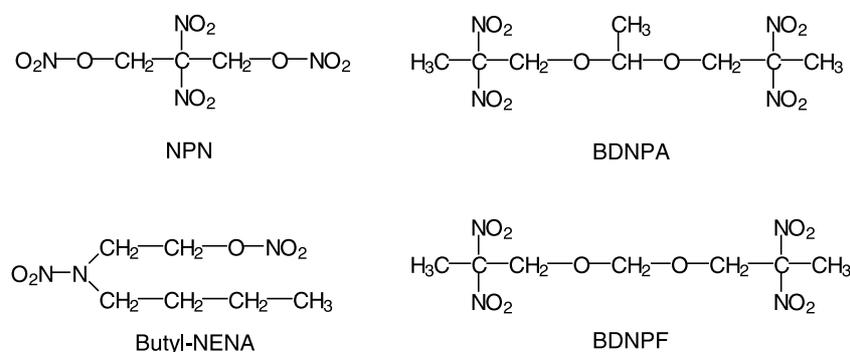
The viscosity of the binder formulations was measured by a Stresstech HR Melt Rheometer at a constant shear rate of 1.0 s⁻¹. The viscosity measurements were done at 30 and 60 °C.

The thermal stability of NPN was determined by measuring the heat flow from approximately 0.5 gram of each sample. The measurements were done isothermally in a Thermal Activity Monitor, TAM 2277, heat flow micro-calorimeter at 65 °C. The samples were put in 3 ml glass ampoules and hermetically sealed with aluminum caps.

The impact sensitivities were determined according to the BAM standard which conforms to the UN guideline ST/SG/AC.10/11⁽⁹⁾, with two exceptions. First, the impact sensitivity was measured with a 2 kg drop weight and second the impact testing was done by using an up-and-down method on both sides of the 50% probability level. For liquid explosives, the gap between the two steel cylinders was 2 mm.

3 Results and Discussion

2,2-Dinitro-1,3-propanediol was synthesized according to a synthetic route described elsewhere⁽¹⁰⁾. It was then nitrated in ordinary mixed acids to form 2,2-dinitro-1,3-bis-nitrooxy-propane (NPN). The elemental analysis of NPN is in good agreement with the theoretical values as shown in Table 1.



Scheme 1. Structure of energetic plasticizers used in this study.

Table 1. Elemental analysis of NPN (wt-%).

	% C	% H	% N	% O
Theoretical	14.07	1.57	21.88	62.48
Experimental	14.05	2.16	21.65	Not measured

NPN is a liquid at room temperature and its structure and some of its properties are presented in Scheme 1 and Table 2. Butyl-NENA and BDNPA/F are used as comparison.

3.1 Lowering of the Glass Transition Temperature

All reported experimental values of glass transitions in this study are based on the temperature in the middle of the transition. This glass transition temperature is called the midpoint, T_{gMid} . Thus T_g in this study is equal to T_{gMid} and calculated according to Eq. (1):

$$T_g = T_{gMid} = \frac{T_{gOn} + T_{gEnd}}{2} \quad (1)$$

where the onset, T_{gOn} , and the endset, T_{gEnd} , of the transition were evaluated at the intercept of the extrapolated tangents as seen in the DSC curve for pure NPN in Figure 1.

In order to study the plasticizing effect of NPN on uncured PolyNIMMO, the glass transition on the respective substance and on mixtures of the two, containing 25, 33 and 50 wt-% NPN, was measured. The results are presented in Figure 2 and in Table 3.

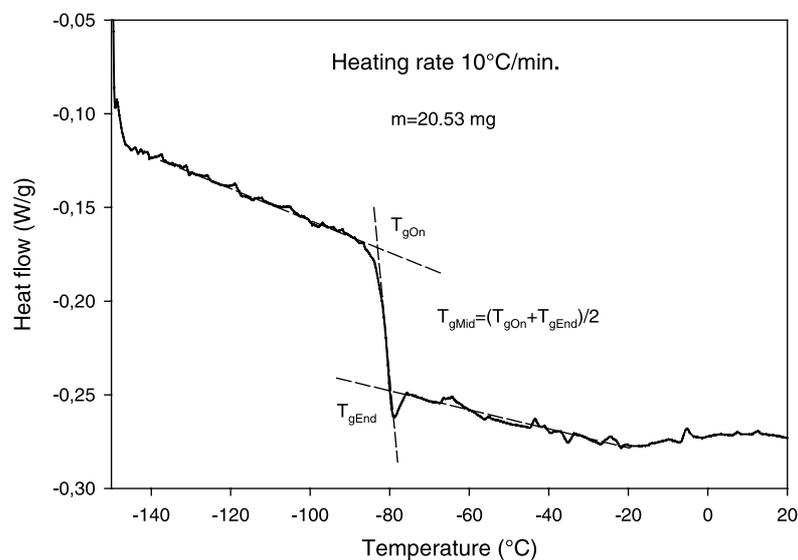
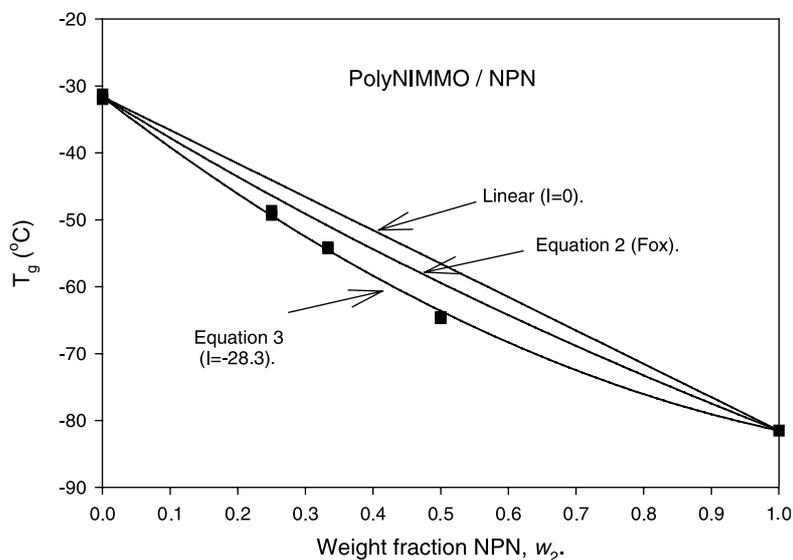
To calculate the glass transition temperature for a binary (single phase) mixture of a polymer and a plasticizer, many empirical equations have been proposed^(12,13). One of the more commonly used is the Fox equation:⁽¹⁴⁾

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

where w is the weight fraction and the index i is for the polymer and 2 is for the plasticizer. Observe that the temperature must be denoted in Kelvin when using the Fox

Table 2. Properties of energetic plasticizers used in this study.

	Butyl-NENA	BDNPA/F	NPN
Sum formula	$C_6H_{13}N_3O_5$	$C_{7.5}H_{13}N_4O_{10}$	$C_3H_4N_4O_{10}$
Mol. weight (g/mol)	207.2	319.2	256.1
Oxygen balance (%)	-104.3	-57.6	+12.5
Density (g/cm ³)	1.22 ^a	1.39 ^a	1.66 ^b
Melting point (°C)	-9 ^a	-15 ^a	Liquid at RT
Enthalpy of formation ^a (kJ/g)	-930	-1940	Not measured

^a) Values from Ref. 11.^b) Value measured by FOI.**Figure 1.** DSC glass transition curve of pure NPN.**Figure 2.** Glass transition temperature of uncured PolyNIMMO plasticized with NPN.

equation. The equation is very useful when only the T_g for respective pure substance is known. The interaction between the polymer and the plasticizer is, however, not taken into account.

To obtain a better fit to the experimental data in this study, the following equation has been used:

$$T_g = T_{g1}w_1 + T_{g2}w_2 + Iw_1w_2 \quad (3)$$

Table 3. Glass transition temperatures of the pure materials and of 50/50 polyNIMMO/plasticizer mixtures and their calculated interaction parameter.

Substance	T_g (°C)	T_g (°C) $w_2=0.5$	I (°C)	s^a (°C)
PolyNIMMO	-31.6	-	-	-
NPN	-81.5	-64.6	-28.3	3.3
Butyl-NENA	-83.5	-70.1	-54.9	3.7
BDNPA/F	-65.2	-48.5	-0.1	0.8

a) Standard deviation for the calculated interaction parameter.

Table 4. The viscosity of uncured 50/50 mixtures of polyNIMMO and different plasticizers at 30 and 60 °C.

Polymer	Plasticizer	Viscosity ^a (Pa · s)	
		30 °C	60 °C
PolyNIMMO	-	45	3.6
PolyNIMMO	Butyl-NENA	0.5	0.2
PolyNIMMO	BDNPA/F	3.1	0.5
PolyNIMMO	NPN	0.8	0.3

a) Measured at a constant shear rate of 1.0 s⁻¹.

Eq. (3) was introduced by Jenckel and Hensch⁽¹⁵⁾ and has been successfully used by Chi to describe uncured and cured mixtures of polymers and energetic plasticizers⁽¹⁶⁾. I is called the interaction parameter and it will roughly correspond to the molecular flexibility of the plasticizer⁽¹⁶⁾, based on its molecular structure, and thus a value of the plasticizers ability to lower T_g is obtained. If I is equal to zero, Eq. (3) will describe a straight line in a T_g versus w_2 plot. In Figure 2 the experimental T_g (midpoint) data for PolyNIMMO/NPN mixtures are shown. Eq. (3) can be rewritten as:

$$I = \frac{T_g - T_{g1}w_1 - T_{g2}w_2}{w_1w_2} \quad (4)$$

By using Eq. (4) the interaction parameter was calculated for each binary composition. Since all tests were performed in duplicate, six values were obtained. The interaction parameter for PolyNIMMO/NPN was then calculated by taking the mean value of the six and was found to be -28.3 °C with a standard deviation, s , of 3.3 °C. A standard deviation of 3.3 °C might seem large but the maximum influence in Eq. (2) will only be 0.8 °C when $w_1 = w_2 = 0.5$. The curve described by Eq. (3) is plotted in Figure 2 by using the calculated interaction parameter.

To compare the plasticizing effect of NPN in PolyNIMMO with other energetic plasticizers the same procedure was repeated with the energetic plasticizers butyl-NENA and BDNPA/F in combination with PolyNIMMO. The results are presented in Figure 3 and in Table 3.

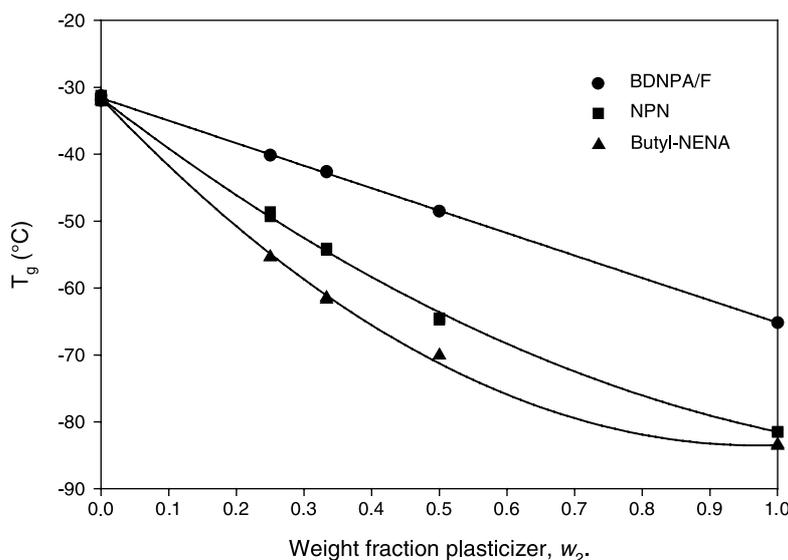
When mixing large amounts of plasticizers in a polymer, phase separation might occur⁽¹⁷⁾. The mixture will then transform into a two phase system, one phase consisting of polymer/plasticizer and the other of plasticizer alone.

At low levels of plasticizers some times a considerably lower depression of the glass transition temperature than expected can be observed, followed by an increase in the modulus at temperatures below the glass transition⁽¹⁸⁾. This phenomenon is referred to as antiplastication.

In none of these two cases will Eq. (3) correctly describe the glass transition temperature of the mixture. We have not studied if Eq. (3) is valid at high (>50%) or low (<25%) levels of plasticizers in PolyNIMMO, since we mainly are interested in the range in between.

3.2 Lowering of the Viscosity

The ability of the plasticizers to lower the viscosity of the polymer was measured on 50/50 mixtures of PolyNIMMO and plasticizer. It was shown that NPN was almost equally effective in lowering the viscosity of PolyNIMMO as butyl-

**Figure 3.** Glass transition temperature of uncured PolyNIMMO with different plasticizers.

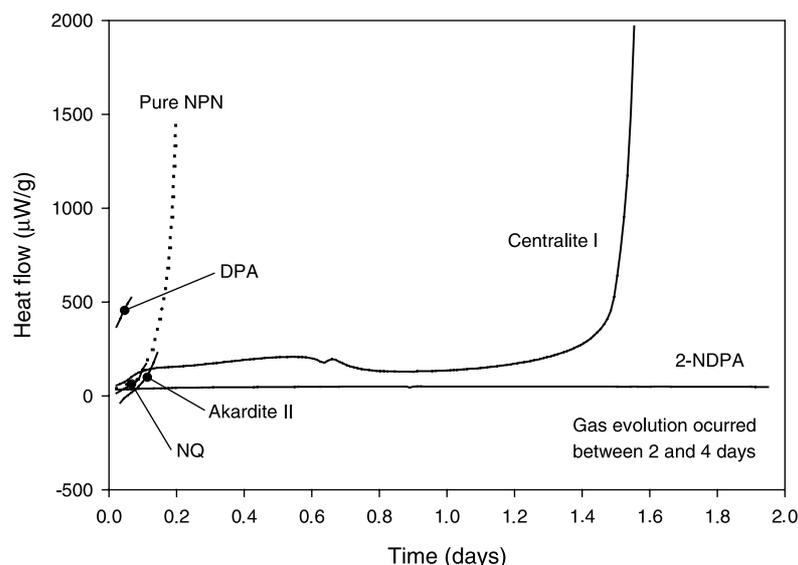


Figure 4. Heat flow during isothermal microcalorimetry of NPN, stabilized with 1% of different stabilizers. Nitroguanidine (NQ), 1,3-diethyl-1,3-diphenylurea (Centralite I), diphenylamine (DPA), 2-nitro-diphenylamine (2-NDPA), 1,1-diphenyl-3-methylurea (Akardite II). Temperature: 65 °C.

NENA (Table 4), which is considered to be very effective in this respect⁽¹⁾.

3.3 Thermal Stability of NPN

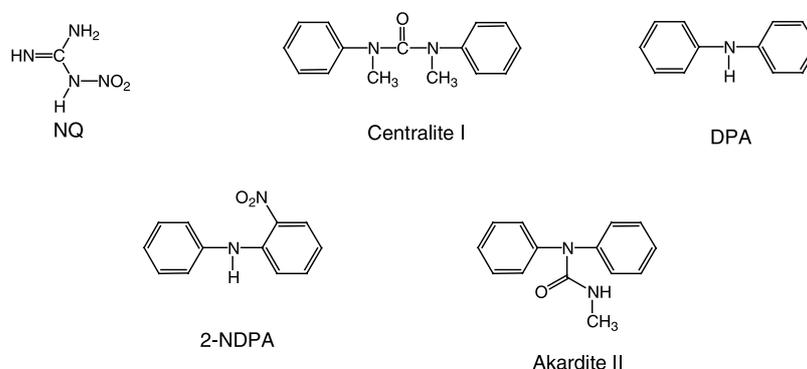
The thermal stability of NPN was measured by microcalorimetry. Pure NPN decomposed within one day at 65 °C. In order to stabilize NPN, different conventional nitrocellulose/nitroglycerine stabilizers were tested (Scheme 2) in combination with NPN at 65 °C.

Figure 4 shows the effect of 1% of different stabilizers on the thermal stability of NPN. Akardite II and DPA have proven to be good stabilizers for nitroglycerine⁽¹⁹⁾, but they had no stabilizing effect on NPN. NQ has shown to be effective in stabilizing NENA compounds in the presence of ammonium perchlorate⁽²⁰⁾. NQ was, however, not useful as a NPN stabilizer, likely due to its insolubility in NPN.

Centralite I and the derivative of DPA, 2-NDPA, was in contrast to DPA the most effective in stabilizing NPN. NPN/Centralite I was stable for one day at 65 °C, whereas NPN/2-NDPA was stable for a minimum of 2 days. Autocatalytic reaction occurred, however, in less than four days.

3.4 Impact Sensitivity

It was found that the impact sensitivity of NPN was lower than 0.2 J which is considered as very sensitive⁽⁹⁾. Due to the high sensitivity of pure NPN the sensitivity of a 50/50 PolyNIMMO/NPN mixture was studied as well, to see if the sensitivity could be improved. The impact sensitivity of the mixture was 2 J (evaluated at 50% probability) which is a substantial improvement but it should still be considered as sensitive.



Scheme 2. Stabilizers used in this study. Nitroguanidine (NQ), 1,3-diethyl-1,3-diphenylurea (Centralite I), diphenylamine (DPA), 2-nitro-diphenylamine (2-NDPA), 1,1-diphenyl-3-methylurea (Akardite II).

4 Conclusions

A new energetic plasticizer, NPN, has been synthesized at FOI. Its plasticizing effect on PolyNIMMO is similar as butyl-NENA. The glass transition temperature of uncured PolyNIMMO was depressed from -32 to -65 °C by adding 50% NPN. NPN was also effective in lowering the viscosity of uncured PolyNIMMO. A drawback of NPN is its thermal instability. Attempts to stabilize NPN with conventional nitrocellulose/nitroglycerine stabilizers have been made, but none of the substances were able to stabilize NPN for more than 2 to 4 days at 65 °C.

5 References

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Acknowledgements

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List of Abbreviations and Symbols

Polymers

PolyNIMMO Poly(3-nitratomethyl-3-methyl oxetane)

Plasticizers

BDNPA Bis(2,2-dinitropropyl)acetal
BDNPF Bis(2,2-dinitropropyl)formal
Butyl-NENA N-n-butyl-N-(2-nitroxy-ethyl)nitramine
NPN 2,2-dinitro-1,3-bis-nitrooxy-propane

Stabilizers

Akardite II 1,1-diphenyl-3-methylurea
Centralite I 1,3-diethyl-1,3-diphenylurea
DPA Diphenylamine
2-NDPA 2-nitro diphenylamine
NQ Nitroguanidine

Symbols

I Interaction parameter used in Eq. (3)
 s Standard deviation
 T_g Glass transition temperature. In this paper $T_g = T_{gMid}$
 T_{gEnd} T_g endset as defined in Figure 1
 T_{gMid} T_g midpoint as defined in Eq. (1)
 T_{gOn} T_g onset as defined in Figure 1
 T_m Melting point
 w Weight fraction

Indices

1 Polymer
2 Plasticizer

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