Improving the Mechanical Properties of Composite Rocket Propellants

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Stockholm 2004

List of Papers

This thesis is based on the following two papers:

1. "Increasing the tensile strength of HTPB with different isocyanates and chain extenders", Wingborg N., *Polymer Testing*, 2002, 21, p. 283-287

2. "2,2-Dinitro-1,3-bis-nitrooxy-propane (NPN): A new energetic plasticizer", Wingborg N. and Eldsäter C., *Propellant, Explosives, Pyrotechnics*, 2002, 27, p. 1-6.

Abstract

Solid composite rocket propellants usually contain ammonium perchlorate embedded in an elastic polymer binder. The binder can be based on a liquid prepolymer such as hydroxyl-terminated polybutadiene, HTPB, or poly(3-nitratomethyl-3-methyl oxetane, PolyNIMMO. HTPB is today widely used for this purpose whereas PolyNIMMO has not yet found its way to an application. Both prepolymers can be cured with diisocyanates to form polyurethane rubber, yielding solid and elastic rocket propellants. It is essential that the solid propellant has good mechanical properties to ensure that the rocket will perform as intended. The propellant must also retain its elastic properties down to the minimum service temperature and thus a low glass transition temperature is important. In fact, the major cause of failure of solid rocket motors is linked to the mechanical properties of the propellants. HTPB has a very low glass transition temperature but in some applications its tensile strength is insufficient. PolyNIMMO, on the other hand, has too high a glass transition temperature and a suitable plasticizer is needed. The purpose of this work is to increase the knowledge of the mechanical properties of polymers by studying how to increase the tensile strength of HTPB and how to decrease the glass transition temperature of PolyNIMMO.

The tensile strength of HTPB was studied by increasing the hard segment content, 1,4-butanediol and 1,4-cyclohexane dimethanol being used as chain extenders. The materials were crosslinked with either isophorone diisocyanate, 1,6-hexamethylene diisocyanate or dicyclohexylmethane 4,4'-diisocyanate. The results show that the tensile strength increase strongly with the addition of up to two moles of diol per mole HTPB. The highest tensile strength was obtained by using dicyclohexylmethane 4,4'-diisocyanate and 1,4-butanediol.

The depression of the glass transition temperature of PolyNIMMO was studied by using a new energetic plasticizer, 2,2-dinitro-1,3-bis-nitrooxy-propane. Two commercial energetic plasticizers, namely bis(2,2-dinitropropyl) acetal/formal and N-N-butyl-N-(2-nitroxy-etyl)nitramine were used for comparison. 2,2-Dinitro-1,3-bis-nitrooxy-propane and N-N-butyl-N-(2-nitroxy-etyl)nitramine were found to interact strongly with PolyNIMMO and they were thus very effective in lowering the glass transition temperature. Bis(2,2-dinitropropyl) acetal/formal on the other hand was not effective, and the depression of the glass transition temperature in this case was due only to dilution of the sample.

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1. List of symbols and abbreviations of chemicals

Symbols

f	Functionality, number of functional groups per molecule (-)
I	Interaction parameter used in equation 3 (°C)
I_{sp}	Specific impulse (Ns/kg)
M	Molecular weight (g/mol)
m	Mass (kg)
p_c, p_e	Pressure in combustion chamber and nozzle exit (MPa)
s	Standard deviation (°C)
T_g	Glass transition temperature. In this work $T_g = T_{g\,midpoint}$ (°C)
T_m	Melting point (°C)
w	Weight fraction (-)
ΔH_f	Enthalpy of formation (kJ/mol)
η	Viscosity (Pa·s)
ρ	Density (g/cm^3)
ϕ_2	Volume fraction solid (-)
ϕ_m	Theoretical maximum volume fraction (-)
Ω	Oxygen balance (%)

Subscripts

1	Polymer or binder
2	Plasticizer or filler
NCO	Diisocyanate
OH	Diol

Chemicals

AP	Ammonium perchlorate
BDNPA	Bis(2,2-dinitropropyl)acetal
BDNPF	Bis(2,2-dinitropropyl)formal
BDO	1,4-Butane diol
BHEB	1,4-Bis(2-hydroxyethoxy)benzene
BKF	2,2′-Methylenebis(4-methyl-6-tertiary-butylphenol)
Butyl-NENA	N-N-butyl-N-(2-nitroxy-ethyl)nitramine
CHDI	*trans*-1,4-cyclohexane diisocyanate
CHDM	1,4-Cyclohexane dimethanol
DDI	Dimeryl diisocyanate
Desmodur-W	Dicyclohexylmethane 4,4'-diisocyanate
DOA	Dioctyl adipate
DOS	Doctyl sebacate
H$_{12}$MDI	See Desmodur-W
HDI	1,6-Hexamethylene diisocyanate
HTPB	Hydroxyl-terminated polybutadiene
IPDI	Isophorone diisocyanate
MDI	4,4'-Diphenylmethane diisocyanate
NPN	2,2-Dinitro-1,3-bis-nitrooxy-propane
PolyNIMMO	Poly(3-nitratomethyl-3-methyl oxetane
TDI	Toluene diisocyanate

2. Introduction

2.1 Purpose of the study

Hydoxyl-terminated polybutadiene, HTPB, is today widely used as binder in solid composite rocket propellants. It combines many attractive physical and chemical properties. In some applications, however, the tensile strength of HTPB-based propellants is insufficient.

Poly(3-nitratomethyl-3-methyl oxetane) (PolyNIMMO), is a new polymer developed solely for use in propellants and explosives. If PolyNIMMO is used, propellants with a higher performance than HTPB-based propellants can be obtained. PolyNIMMO-based propellants are still in the development phase and they have not found their way into any commercial application. One property that must be improved is its high glass transition temperature.

The purpose of this work is to improve the knowledge in the field of polymer technology by studying how the tensile strength of HTPB can be increased without decreasing the ultimate elongation, and how the glass transition temperature of PolyNIMMO can be decreased without reducing the performance of the propellant.

2.2 Processing and performance of solid rocket propellants

Rocket propellants usually contain a crystalline oxidizer embedded in an elastic polymer matrix [1,2]. This type of propellant is called a composite propellant and the solid oxidizer of choice has, for at least 40 years, been ammonium perchlorate, AP (NH_4ClO_4). The purpose of the polymer matrix, also known as the binder, is to form a solid, elastic body of the propellant ingredients with sufficient mechanical properties. The binder is also used as a fuel since it contains mainly hydrogen and carbon. Good mechanical properties are essential to assure that the rocket will perform as intended. In fact, the major cause of failure in solid rocket motors is linked to the structural integrity of the propellant [1].

The most well-known polymer used in composite propellants is liquid hydroxyl-terminated polybutadiene, HTPB, cured with diisocyanate [2,3]. Propellants based on AP and HTPB have a number of desirable properties, such as a low glass transition temperature, sufficient mechanical properties and high performance.

In the manufacture of a propellant, the solid ingredients (mainly AP) are mixed into the liquid prepolymer. The mixture is then cast in a mold and cured at an elevated temperature. In this way, a solid and elastic propellant with the desired shape is formed. The viscosity of the uncured propellant, η, must be low enough to allow casting and the pot life must be long to achieve good mixing. If the volume fraction of the solid, ϕ_2, is increased, the viscosity increases as seen in Figure 1, based on the modified Roscoe equation [4], where η_l is the viscosity of the uncured liquid binder and ϕ_m is the theoretical maximum volume fraction of randomly close-packed monomodal spheres and is equal to 0.63 [4]. When ϕ_2 approaches ϕ_m, the viscosity increases dramatically and a solid loading of 0.63 cannot be obtained with monomodal spheres.
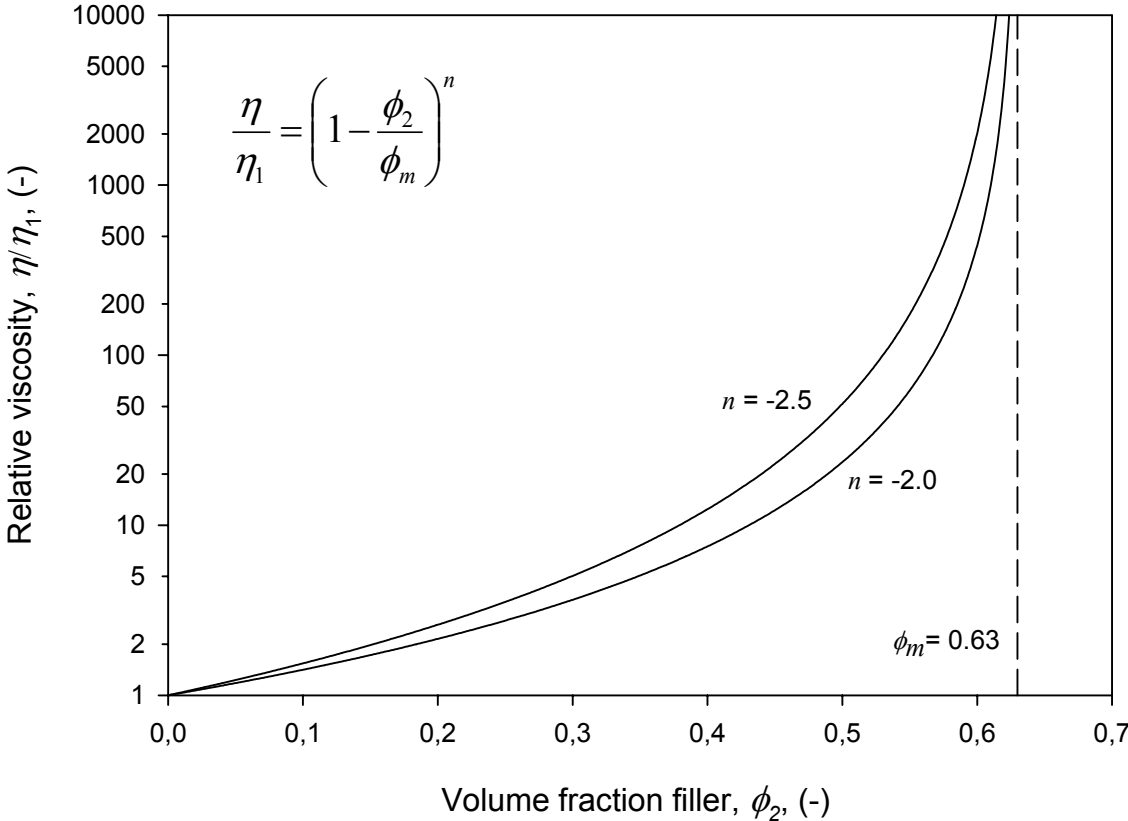

Figure 1. Relative viscosity vs vol. fraction of randomly packed monomodal spheres.

The specific impulse, I_{sp}, is a measure of the performance of a rocket propellant and is expressed in Ns/kg. If the chemical composition and heats of formation of the ingredients in the propellant are known, I_{sp} can be calculated. By using the data in Table 1 and the Cheetah 2.0 thermochemical computer code [5], I_{sp} values for AP/HTPB-based propellants with different amounts of AP were calculated. The results are shown in Figure 2.

Table 1. Data[a] for the components used in the thermochemical calculations.

	Sum formula	Ω (%)	ΔH_f (kJ/mol)	ρ (g/cm^3)
HTPB	C_4H_6	-325	0	0.90
PolyNIMMO	$C_5H_9NO_4$	-114	-309	1.26
AP	NH_4ClO_4	+34	-296	1.95

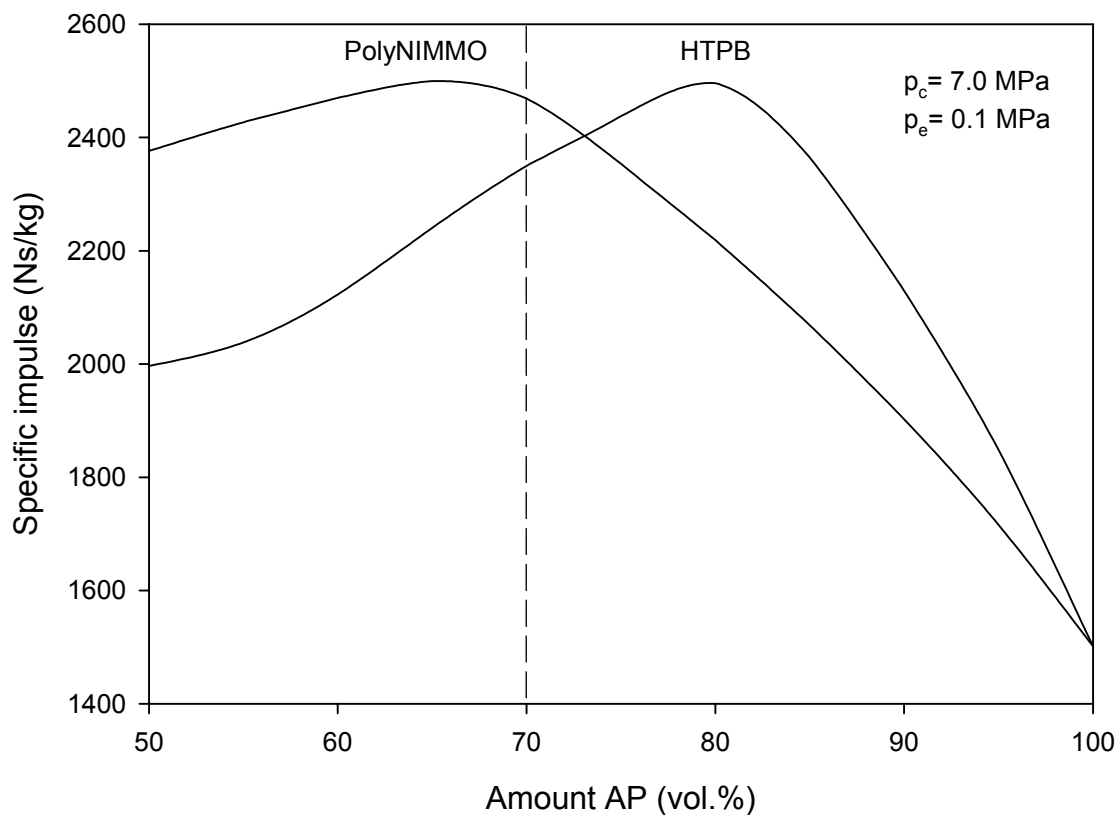*a*) Data from references [5] and [6].

Figure 2. Specific impulse as a function of the amount of AP.

Figure 2 shows that the maximum specific impulse for an AP/HTPB-propellant is obtained at 80 volume % AP. Such a high solid loading cannot be achieved with a monomodal particle size, as is shown in Figure 1. Bimodal or trimodal particle sizes are thus often used but it is still very difficult to achieve a volume solid loading of 80%. Experience at FOI has shown that a reasonable maximum solid loading in a bimodal AP/HTPB-propellant is 70 volume % of AP. This is shown as a broken line in Figure 2. At higher amounts of AP, the processing of the propellant becomes very difficult. Using energetic polymers, such as poly(3-nitratomethyl-3-methyl oxetane) (PolyNIMMO) [7,8], it is possible to increase the specific impulse of a solid rocket propellant since the optimum composition in this case is found at a solids loading below 70 volume %, as seen in Figure 2. Note that the peak value of the specific impulse is about the same for the HTPB- and PolyNIMMO-based propellants. The difference between using energetic and non-energetic polymers is that the peak in Figure 2 is shifted along the abscissa. Figure 3 shows the structure of PolyNIMMO, and it can be seen that it contains one nitro ester group per repeating unit. The oxygen balance for PolyNIMMO is thus much higher than for HTPB, as shown in Table 1, and for this reason PolyNIMMO requires less solid oxidizer to reach its maximum specific impulse.
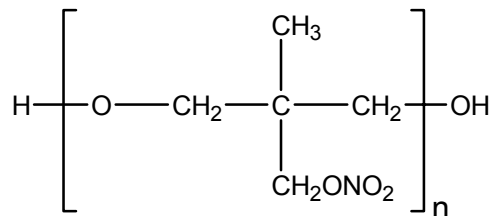

Figure 3. Structure of PolyNIMMO [7,8].

2.3 Tensile properties

It is not unusual to require an ultimate elongation of 50% from the propellant, especially when the propellant is case-bonded [1,9]. This means that the elongation of the binder itself must be about 500% [1]. In some applications, as in very high accelerating, or gun-launched rockets, propellants with a high tensile strength are needed. HTPB has a zig-zag molecular arrangement due to its the *cis-trans*-morphology. This makes close packing of the molecules difficult, and the polymer is amorphous and transparent. The interchain forces are weak since the repeating unit contains only hydrogen and carbon atoms. As a result, the tensile strength of cured HTPB is very low. Increasing the tensile strength should preferably not be done at the expense of the ultimate elongation, as occurs when the crosslink density in HTPB is increased using trifunctional alcohols such as trimethylol propane [9,10] or triethanol amine [11], or by increasing the isocyanate/hydroxyl (NCO/OH) equivalent ratio [11-14].

The tensile properties can be altered to some extent by curing HTPB with different isocyanates such as DDI, HDI, H_{12}MDI, IPDI, MDI and TDI, but the tensile strength is in general poor and of the order of 1 MPa or below [12-17]. One exception is CHDI which, when used to cure HTPB, yields a polyurethane with a tensile strength of 2 MPa and an ultimate elongation of 190% [15].

Polyurethane elastomers contain soft and rigid segments. The soft segments consist of the flexible non-crystalline polymer chains, in this case polybutadiene, and the rigid or hard segments consist of diisocyanate residues, chain extenders and urethane groups. Segregation and phase separation of the soft and rigid segments in HTPB has been studied [18-20]. The tensile strength of curable polyurethanes can be increased by increasing the number of urethane bonds and by using symmetrical and rigid molecules in the hard segments [4,18,21-24]. With increasing number of urethane bonds, the interchain forces increase due to larger amount of hydrogen bonds between the polymer chains. The amount of urethane bonds can be increased by adding low molecular weight diols to the polymer and by increasing the amount of diisocyanate. These types of diols are often called chain extenders. The most common aliphatic diol for this purpose is 1,4-butanediol, BDO [23]. Diamines are also widely used as chain extenders in liquid polyurethanes [4,22]. Their high reactivity gives a short pot life and for this reason they have not found any applications in the production of propellants.

The more symmetric the diisocyanates and the chain extenders molecules are, the easier will the hard segments crystallize [22]. If the hard segments contain bulky aromatic or cyclo-aliphatic groups, the rigidity will increase and lead to interchain steric hindrance. If the interchain forces are increased, the crystallinity and rigidity of the hard segments and the potential for macromolecular slippage will decrease. This will influence the mechanical properties mainly by increasing the modulus of elasticity and the tear and tensile strengths [4,22,25].

HTPB mixed with BDO and cured with the diisocyanates CHDI, DDI, HDI, MDI and TDI has been studied [13,15,17,18]. Aliphatic diisocyanates are generally less reactive than aromatic [22], and aliphatic diisocyanates are thus preferred in the production of rocket propellants when a long pot life is desired. A common diisocyanate to cure HTPB-based propellants is isophorone diisocyanate, IPDI. In this work, the mechanical properties of HTPB/IPDI/BDO mixtures were examined. IPDI is a non-symmetrical cycloaliphatic isocyanate. Since symmetrical diisocyanates gives higher strength, mixtures with a symmetrical cycloaliphatic diisocyanate, dicyclohexylmethane diisocyanate, $H_{12}MDI$ or Desmodur W, were also studied.

In the work of Minoura *et al.* [26,27], several different aromatic and cycloaliphatic diols with high melting point (105-170°C) were used as chain extenders in combination with HTPB. The materials were cured with MDI, yielding materials with a tensile strength in the range of 5 to 6 MPa. Low melting point diols are however preferred in order to make the processing easier. In this work, a low melting point cyclo-aliphatic diol, 1,4-cyclohexane dimethanol, CHDM, (T_m= 31.5°C) has also been used.

Figure 4 shows a stress-strain curve for PolyNIMMO. Both the tensile strength and the ultimate elongation are rather high. The mechanical properties are however strongly altered by the introduction of a plasticizer [28]. Thus before an attempt can be made to improve the tensile properties of PolyNIMMO, a suitable plasticizer must first be identified.
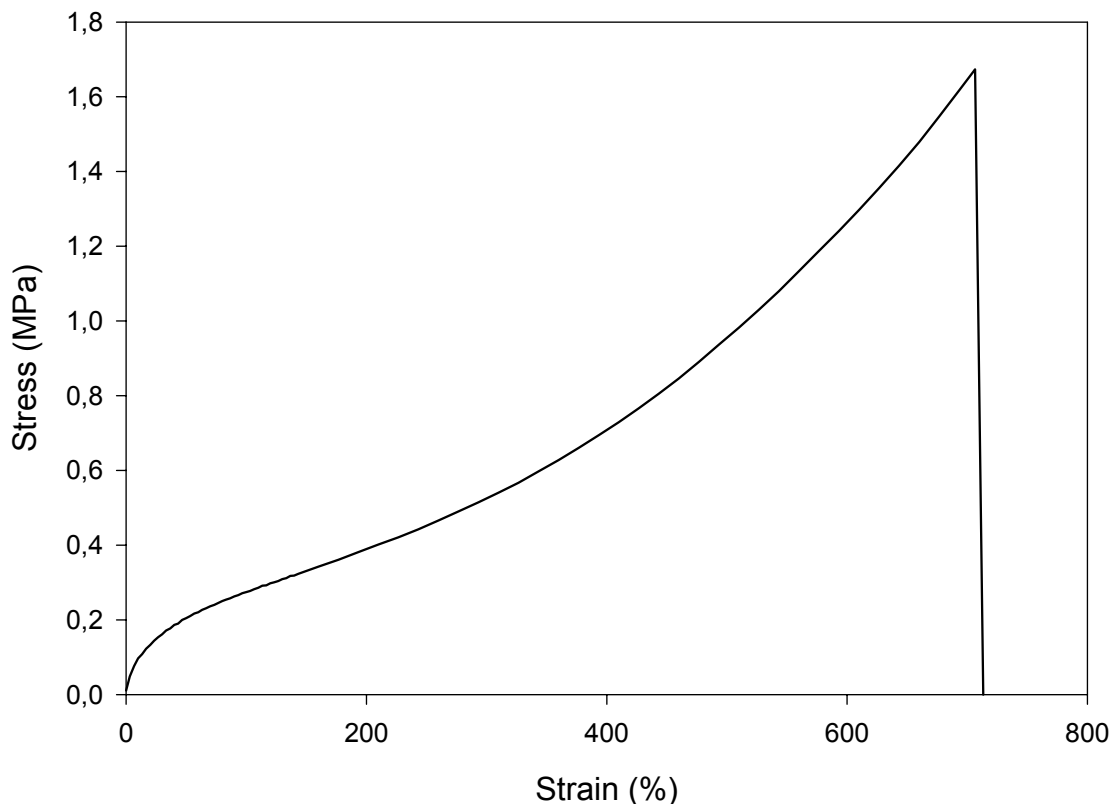
Figure 4. Stress-strain curve of cured PolyNIMMO. From reference [28].

2.4 Glass transition temperature

A propellant must maintain its elastic properties within the intended operational temperature range. This means that the glass transition temperature of the binder must be lower than the minimum service temperature (usually –40 to –54°C depending on the application) [2,29] in order to avoid failure of the motor during firing at low temperatures. Cured HTPB has a glass transition temperature of approximately -70°C [15] and its glass transition temperature is not therefore a matter of concern. Nevertheless, plasticizers such as DOS and DOA are sometimes used in HTPB-propellants to lower the viscosity of the uncured propellant. This improves the processing and thus the specific impulse as shown in Figures 1 and 2. Increasing the tensile strength by increasing the amount of hard segments in HTPB will not, fortunately, alter the glass transition to any great extent. This is probably because of almost complete phase separation between the hard and the soft segments [19,30].

Uncured difunctional PolyNIMMO has a glass transition temperature ranging from -15°C [29,31] to -25°C [8,32,33] and -30°C [34]. In some of the reports, it was not clear whether the polymer was cured or not and since, in general, the glass transition increases by 10°C when the polymer is cured [29], this or batch variations might explain the large variations. The glass transition temperature of PolyNIMMO is in all cases higher than the minimum service temperature and it must therefore be lowered to meet the requirements. This can be done by using a suitable plasticizer. Using non-energetic plasticizers such as DOS and DOA will however shift the maximum specific impulse in Figure 2 to a higher AP content and the benefit of using PolyNIMMO is thus decreased. To obtain a high specific impulse it is desirable to use energetic plasticizers in combination with PolyNIMMO. The difference between a non-energetic and an energetic plasticizer is that the energetic ones contain e.g. nitro, nitro esters, nitramine or azide functional groups. The presence of these functional groups makes the energetic plasticizers polar and in general they thus have a poor physical compatibility with non-polar polymers like HTPB.

A good plasticizer should have a low glass transition temperature, a low viscosity and a low tendency to migrate [29,35]. An energetic plasticizer should also have a high oxygen balance, a low impact sensitivity and a high thermal stability. These demands are in many cases contradictory and it is not easy to find the ultimate energetic plasticizer. Several energetic plasticizers such as nitratoethyl nitramines (NENAs) [29,32,35-37], nitrate esters (*e.g.* nitroglycerine, butanetriol trinitrate (BTTN) and trimethylolethane trinitrate (TMETN)) [31], azido compounds [31,38,39], bis(2,2-dinitropropyl)acetal/bis(2,2-dinitropropyl)formal (BDNPA/F) [29,32,35,40], nitroaromatic compounds (*e.g.* 2,4-/2,6-dinitroethylbenzene/2,4,6-trinitroethylbenzene) [29,35] and nitrato oligomers (glycidyl nitrate and NIMMO oligomers) [33], 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 [41]. This work shows how the energetic plasticizers NPN, butyl-NENA and BDNPA/F alter the glass transition temperature of PolyNIMMO. Since NPN is a new energetic plasticizer, some of its properties have also been characterized.

3. Experimental

3.1 Materials

The chemicals used in this study can be divided into five different groups, namely polymers, antioxidants, diisocyanates, chain extenders and plasticizers. They were all used as received without any further purification.

Polymers

- Hydroxyl-terminated polybutadiene, HTPB, R-45HT (ARCO, USA) [24];
- PolyNIMMO BX PP880 , poly(3-nitratomethyl-3-methyl oxetane), 2-functional, (Nobel Enterprises, UK) [42].

Antioxidant

- 2,2´-Methylene-bis-(4-methyl-6-tertiary-butylphenol), BKF, from Bayer AG, Germany.

Diisocyanates

- Isophorone diisocyanate, IPDI, (Hüls AG, Germany);
- Dicyclohexylmethane 4,4´-diisocyanate, $H_{12}MDI$ or Desmodur W, (Bayer AG, Germany);
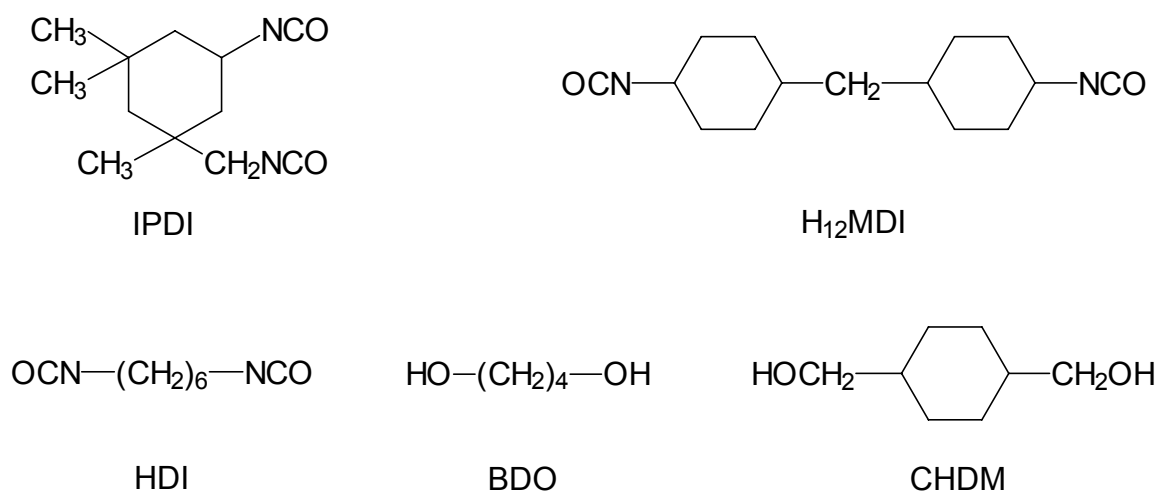- 1,6-Hexamethylene diisocyanate, HDI, (Ventron GMBH, Germany).

Figure 5. Chemical structure of the diisocyanates and chain extenders used.

Chain extenders

- 1,4-Butanediol, BDO, (Janssen Chimica, Belgium);
- 1,4-Cyclohexane dimethanol, CHDM, (Janssen Chimica, Belgium).

Table 2 shows data for the materials used to improve the tensile properties of HTPB. The functionality, f, is defined as the number of reactive groups per molecule that participate in the reaction to form urethane bonds.

Table 2. Data for materials used to improve the tensile properties.

Materials	Functionality, f	Molecular weight, M	Comments
HTPB	2.3	2700	Type R-45 HT [24]
IPDI	2	222	Mixture of isomers
H_{12}MDI	2	262	Mixture of isomers
HDI	2	168	Volatile
BDO	2	90	Very hygroscopic
CHDM	2	144	Melting point 31.5 °C

Plasticisers

- Butyl-NENA, N-*n*-butyl-*N*-(2-nitroxy-ethyl)nitramine, (DYNO 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).

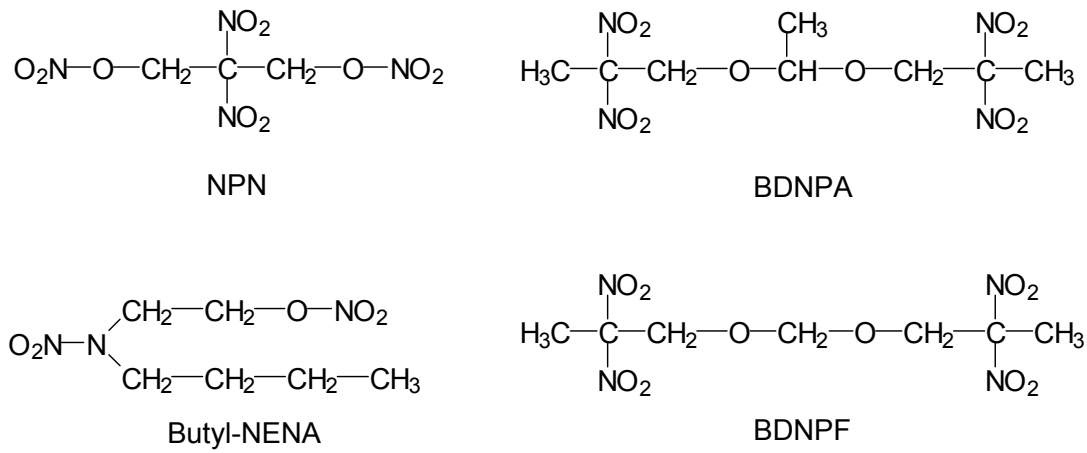The chemical structures of the plasticizers are shown in Figure 6.

$O_2N-O-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-O-NO_2$

$H_3C-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-O-\overset{\overset{CH_3}{|}}{CH}-O-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_3$

NPN

BDNPA

$O_2N-N\overset{\diagup CH_2-CH_2-O-NO_2}{\diagdown CH_2-CH_2-CH_2-CH_3}$

$H_3C-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-O-CH_2-O-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_3$

Butyl-NENA

BDNPF

Figure 6. Structure of energetic plasticizers used in this work.

3.2 Methods

All the mixtures based on HTPB, diisocyanate and diol, were mixed by hand in a beaker. The total weight of each batch was 30 g. Since HTPB is easily subjected to oxidative degradation 2 % of BKF was added as antioxidant. The antioxidative effect of BKF is reported elsewhere [43]. After mixing vigorously for 5 minutes, the beaker was put into a vacuum vessel and the mixtures were degassed until no bubbles were left. The mixture was then cast between Teflon-coated metal plates to form a 2 mm thick sheet and the sheet was cured for one week at 70°C.

In all the mixtures, a stoichiometric quantity of diisocyanate was used, i.e. the NCO/OH ratio was equal to unity. The amount of diisocyanate to be added was calculated from the following equation:

$$m_{NCO}\frac{f_{NCO}}{M_{NCO}} = m_{HTPB}\frac{f_{HTPB}}{M_{HTPB}} + m_{OH}\frac{f_{OH}}{M_{OH}} \tag{1}$$

where f is the functionality, M the molecular weight and m is the mass. The subscripts OH refer to diol and NCO to diisocyanate. The hard segment content was calculated as the mass fraction of diol and diisocyanate in the material.

The tensile strength, the ultimate elongation and the modulus were measured on an Instron Universal Testing Machine, model 5565, according to ISO/R 37-1968, i.e. at room temperature and at a constant strain rate of 500 mm/minute. No extensiometer was used, but the initial length of the test samples was set to 30 mm and the elongation was then calculated. The initial modulus of elasticity was defined as the secant modulus between 10 and 20% of elongation.

The tensile test samples were of type 2, ISO/R 37-1968, and were cut from the cast film with a cutter. The width of the samples was set to 4 mm, which is the width of the cutter tool, and the thickness was measured. Prior to the tensile testing, the samples were stored for more than one week at room temperature. All reported results for the tensile strength, ultimate elongation and initial modulus are averages of six measured values. The standard deviations are presented in the figures by error bars. In some cases, the standard deviation is small and the error bars are thus not seen since they are hidden under the symbols (●○▼▽).

The glass transition temperature was measured using a Mettler DSC 30, differential scanning calorimeter, equipped with a ceramic sensor. All tests and the calibration were performed in a nitrogen atmosphere (50 ml/min) at a heating rate of 10 K/min. The samples were put in 40 µl aluminium 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. All reported experimental glass transition temperatures in this study are the temperature in the middle of the transition i.e. $T_g = T_{g, midpoint} = \frac{1}{2}(T_{g, onset} + T_{g, endset})$.

Elemental analysis was made by H. Kolbe Mikroanalytisches Laboratorium, Mülheim, Germany and the viscosities of the binder formulations were measured on a Stresstech HR Melt Rheometer at a constant shear rate of 1.0 s^{-1} at 30 and 60°C. Densities were measured at room temperature using a precision syringe (50 µl) and a micro balance.

4. Results and discussion

4.1 Altering the tensile strength of HTPB

The hard segment content in the materials varied from approximately 10%, without any diol, to approximately 40%, with 4 moles of diols per mol HTPB. Figures 7 and 8 show typical tensile test curves for HTPB/H_{12}MDI/BDO- and HTPB/IPDI/BDO-based materials. The tensile test curves for the materials containing CHDM were very similar and are thus not shown.

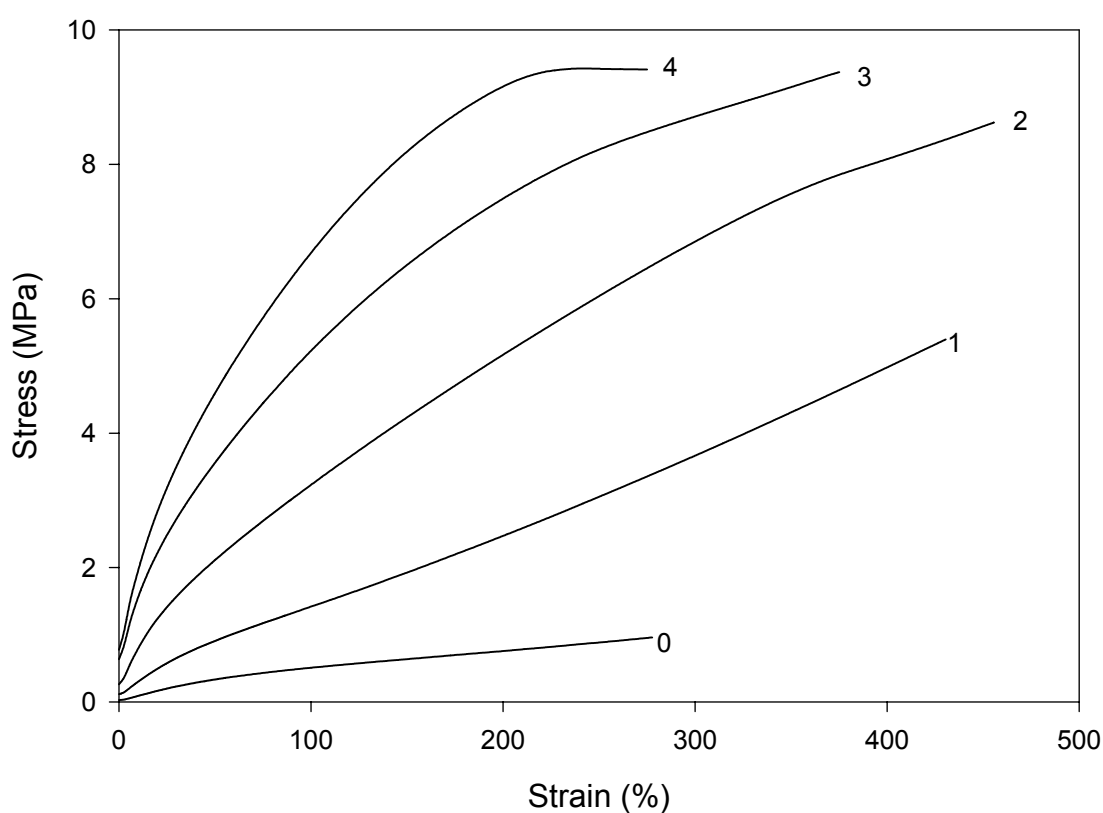**Figure 7.** Tensile test curves for HTPB/H_{12}MDI/BDO-based materials. The numbers indicate the number of mole diols per mole HTPB.

The initial stress values in Figures 7 and 8 are due to the fixation of the samples in the testing machine and increased with increasing stiffness of the sample tested.
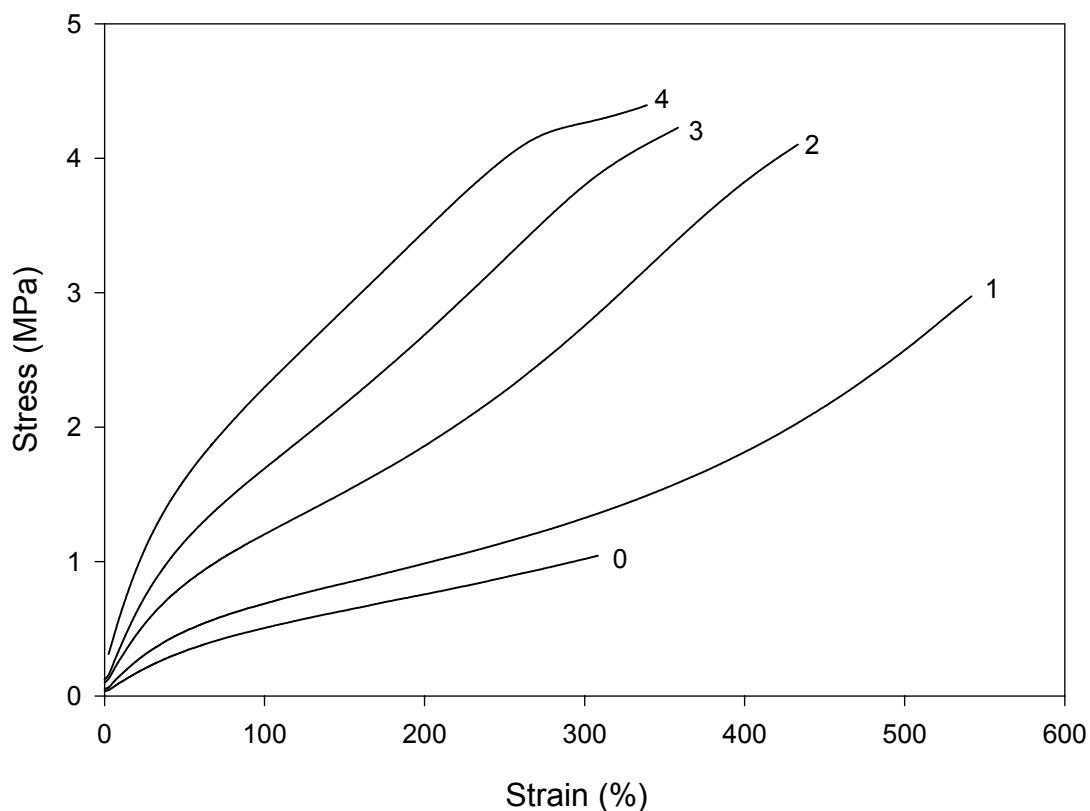
Figure 8. Tensile test curves for HTPB/IPDI/BDO-based materials. The numbers indicate the number of mole diols per mole HTPB.

To obtain a better view of the influence of the different types and amounts of diols and diisocyanates on the mechanical properties, the results are presented in Figures 9 to 11 to show the influence on the tensile strength, ultimate elongation and initial modulus respectively.

Without any diol, the tensile strength is independent of whether $H_{12}MDI$ or IPDI is used, as is clearly shown in Figure 9. When HTPB was cured with HDI, a somewhat lower tensile strength was obtained (0.9 MPa). The poor tensile strength, close to 1 MPa, independent of the diisocyanate used was in good agreement with other studies [12-17].

The number of urethane bonds is not affected by the choice of diisocyanate and the hard segment content is altered to only a slight extent (9.9%, 8.5% and 6.6% for $H_{12}MDI$, IPDI and HDI respectively). This may explain why the tensile strength is hardly influenced.
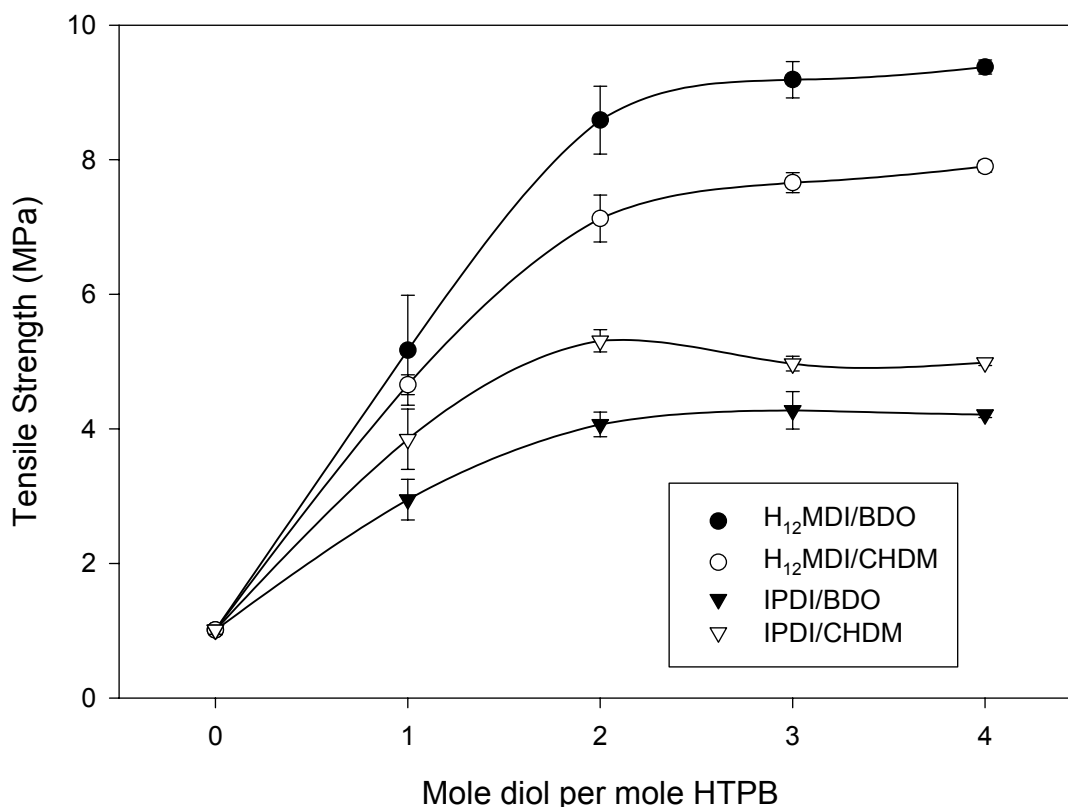
18

Figure 9. Tensile strength as a function of amount of diol for selected compositions.

When the amount of hard segment was increased, more polyurethane bonds were formed and the interchain forces increased, leading to a higher tensile strength as shown in Figure 9. Increasing the amount of hard segments also leads to a higher content of crystalline material. When a chain extender is used, the choice of diisocyanate obviously has a strong effect on the mechanical properties. It is evident in Figure 9 that materials containing H_{12}MDI have a higher tensile strength. This is probably because the more rigid molecular structure of H_{12}MDI prevents chain slippage, while its molecular symmetry promotes crystallization.

It is interesting to note that, in combination with H_{12}MDI, BDO is more effective in improving the tensile strength than CHDM. With IPDI, however, this relation is reversed. The influence on the tensile strength of increasing the amounts of diol and diisocyanate is very strong up to two moles of diol per mole of HTPB. When more diol and diisocyanate are added, the materials start to yield when stretched, and therefore the tensile strength does not increase.

When HTPB/BDO was cured with HDI using two moles BDO per mole of HTPB, a stiff and opaque material was formed. Its tensile strength was 5.0 MPa but the ultimate elongation was only 220% which is low compared to that of the other materials as seen in Figure 10. The linear structure and the flexibility of HDI and BDO probably promote a high degree of crystallization in the hard segment. Since, in this case, high ultimate elongation is preferred, no further experiments were made using HDI. All the other combinations of diisocyanates and diols in HTPB yielded materials which were transparent.
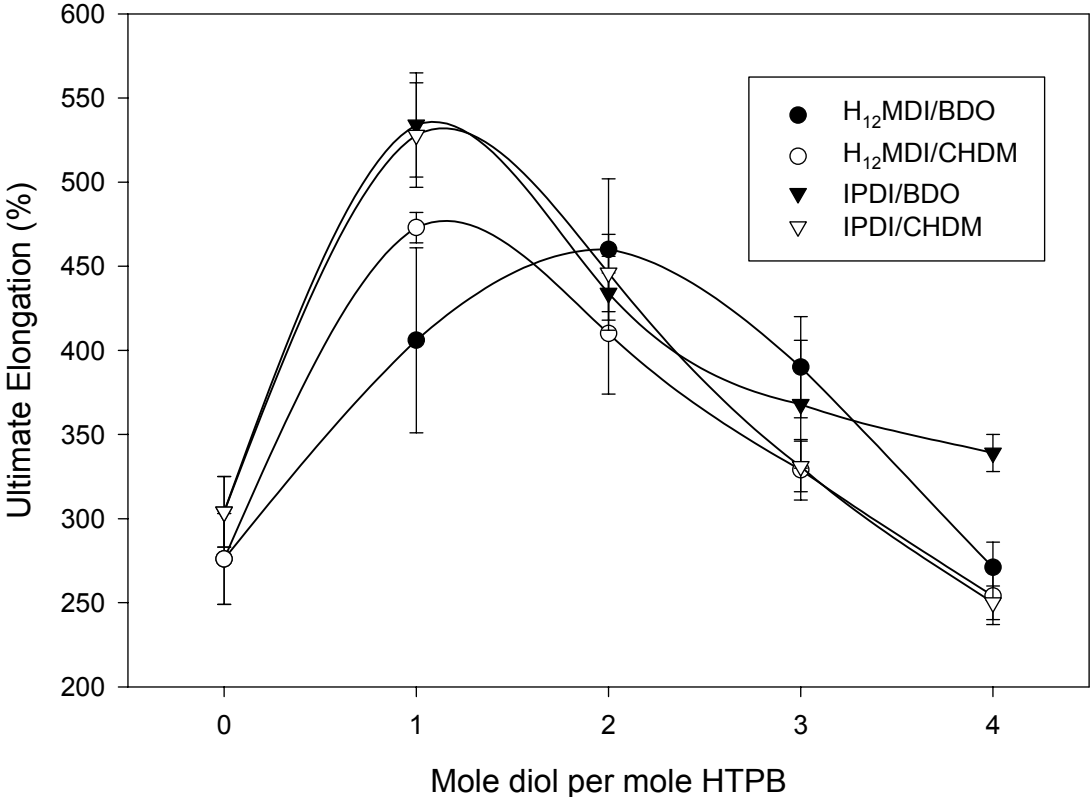

Figure 10. Ultimate elongation as a function of the amount of diol for selected compositions.

Figure 10 shows the ultimate elongation of the materials. The influence of the different diisocyanates and diols on the ultimate elongation is less than on the tensile strength. All materials have a maximum elongation with between one and two moles of diol per mole of HTPB. The most elastic material is obtained with IPDI and one mole of diol per mole HTPB. With a larger amount of hard segment in the materials, the tensile strength increases and the materials will not rupture as easily, and they can thus survive being stretched to a higher degree. The modulus increases with increasing amount of diisocyanate and diol, as shown in Figure 11. This is of course also due to the increase in the hard segment content. With larger amounts of hard segment the increase in modulus is more pronounced then the increase in

tensile strength. This leads to a decrease in the elasticity of the materials, as shown in Figure 10.

At diol concentrations above one mole per mole of HTPB, all the materials formed strain-induced crystals, which was clearly observed as an increase in opaqueness of the samples. To strain crystallize, the materials must have a tensile strength high enough to survive being stretched to the point at which strain-induced crystals can be formed. In this case, this limit seems to be in the region of 1-2 MPa. When chain extenders are used, the modulus increases linearly with increasing molar content, Figure 11. The stiffest materials were those containing $H_{12}MDI$ and BDO. When IPDI was used, CHDM gave a more rigid material than BDO. This behavior is in agreement with the influence of diol on the tensile strength.
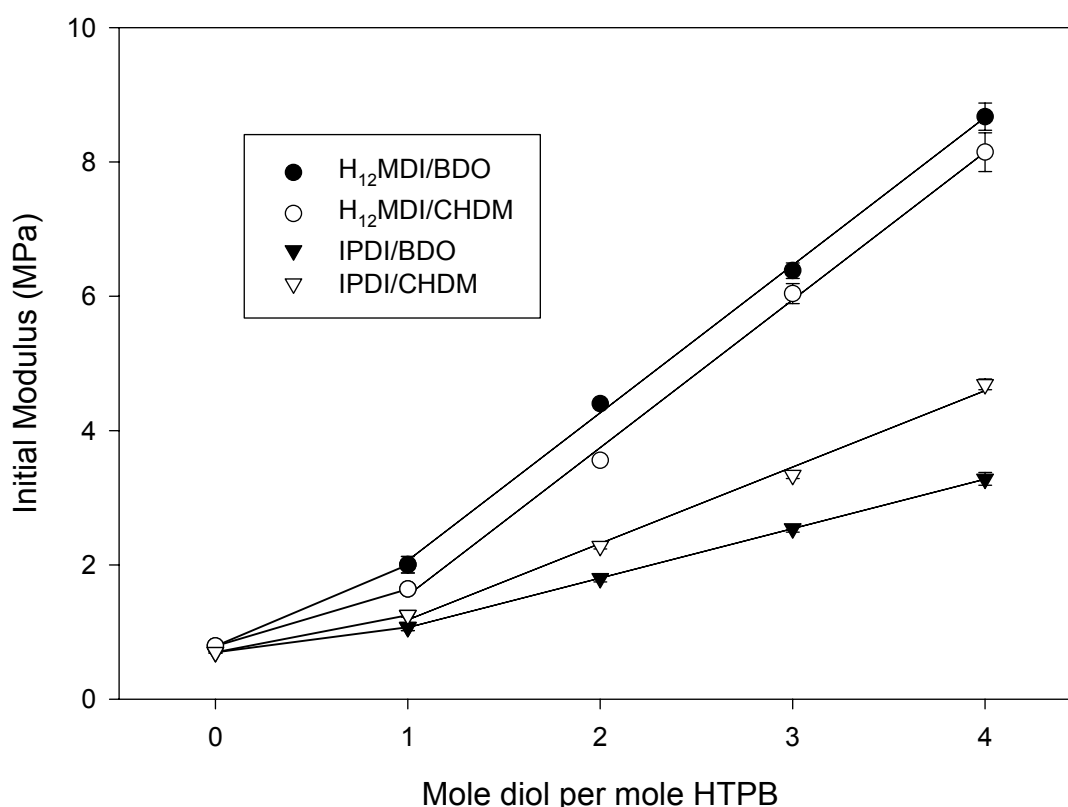

Figure 11. Initial modulus as a function of the amount of diol for selected compositions.

Rigid and bulky diols and diisocyanates increase the tensile strength by hindering molecular slippage. The ability to crystallize decreases, however, with increasing rigidity of the hard segments. The maximum tensile strength is thus obtained using hard segments that have a rigidity intermediate the values favoring each of the two physical processes. This may be the reason why CHDM with $H_{12}MDI$ has a lower tensile strength than BDO with $H_{12}MDI$. IPDI

is less bulky than $H_{12}MDI$ and, in combination with CHDM, the tensile strength increases more than if BDO is used.

In order of decreasing modulus and decreasing tensile strength the materials are:

$H_{12}MDI/BDO > H_{12}MDI/CHDM > IPDI/CHDM > IPDI/BDO$

In order of decreasing bulkiness of the hard segments the materials are:

$H_{12}MDI/CHDM > H_{12}MDI/BDO > IPDI/CHDM > IPDI/BDO$

Several studies have been made on HTPB and different diisocyanates, using BDO as chain extender [13,15,17]. As can be seen in Table 3, $H_{12}MDI$ gives the highest tensile strength. It is somewhat surprising that diisocyanates of rather similar structure, such as $H_{12}MDI$ and MDI, and IPDI, CHDI and TDI, yield materials with such a large difference in strength. From these studies it seems that an aliphatic diisocyanate gives a higher tensile strength than an aromatic one.

Table 3. Tensile strength of HTPB with one mole BDO per mole HTPB.

Diisocyanate	Tensile strength (MPa)	Reference
CHDI	4.3	[15]
DDI	1.0	[15]
HDI	2.4^a	[13,15,17]
$H_{12}MDI$	5.2	b
IPDI	3.0	b
MDI	3.5	[17]
TDI	1.9	[17]

a) Average from the three references.

b) Data from this study.

It is possible to further increase the tensile strength of HTPB-based polyurethanes by using a more rigid chain extender. The highest tensile strength of materials of the HTPB/diisocyanate/diol type found in the literature are listed in Table 4.

Table 4. Properties of HTPB/diisocyanate/diol. One mole diol per mole HTPB.

Diisocyanate/diol	Tensile strength (MPa)	Ultimate elongation (%)	Melting point of diol (°C)	Reference
H_{12}MDI/BDO	5.2	400	16	*a*
H_{12}MDI/CHDM	4.7	470	32	*a*
MDI/Hydroquinone	5.5	100	170	[26]
MDI/Bisphenol-A	5.9	150	157	[26]
MDI/BHEB	6.2	150	105	[27]

a) Data from this study.

The highest tensile strength is obtained using MDI and hydroquinone, bisphenol-A or BHEB as chain extender. Unfortunately from a processing point of view, hydroquinone, bisphenol-A and BHEB all have a very high melting point, which makes the processing more complicated. They also give materials with rather low ultimate elongation. In this comparison, materials with H_{12}MDI and BDO or CHDM seem very attractive, yielding materials with a fairly high tensile strength and a very high ultimate elongation.

Bisphenol A (2,2-Bis(4-hydroxyphenyl)propane)

Hydroquinone (1,4-Benzenediol)
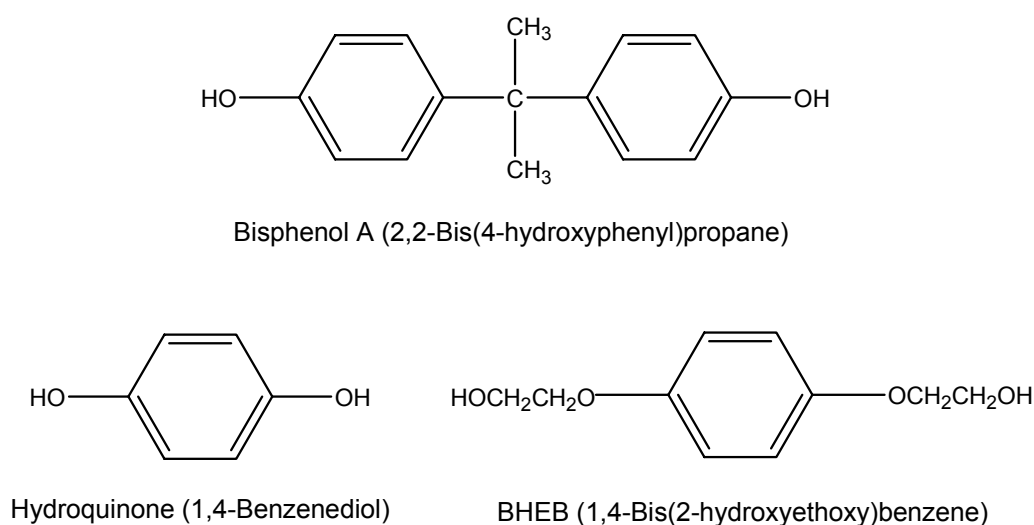
BHEB (1,4-Bis(2-hydroxyethoxy)benzene)

Figure 12. Structure of some of the chain extenders listed in Table 4.

4.2 Altering the glass transition temperature of PolyNIMMO

2,2-dinitro-1,3-propanediol was synthesized according to a synthetic route described elsewhere [44]. It was then nitrated in a mixture of nitric and sulfuric acid to form 2,2-dinitro-1,3-bis-nitrooxy-propane, NPN. The elemental analysis of NPN was in good agreement with the theoretical values as shown in Table 5.

Table 5. Elemental analysis of NPN (weight-%).

	%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 some of its properties are presented in Table 6. Butyl-NENA and BDNPA/F are used as comparison.

Table 6. Properties^a 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	1.39	1.66^b
Melting point (°C)	-9	-15	Liquid at RT
Enthalpy of formation (kJ/g)	-930	-1940	Not measured

a) Values from reference [6] unless otherwise stated.

b) Value measured at FOI.

In order to study the plasticizing effect of NPN on uncured PolyNIMMO, the glass transitions of each substance and of the mixtures of the two containing 25, 33 and 50wt% NPN were measured. The results are presented in Figure 13 and in Table 7.

To calculate the glass transition temperature for a binary (single phase) mixture of polymer and plasticizer, many empirical equations have been proposed [4,45]. One of those more commonly used is the Fox equation [46]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

(2)

where w is the weight fraction and the index 1 is for the polymer and 2 is for the plasticizer ($w_1 + w_2 = 1$) and T is the temperature in Kelvin. The equation is very useful when only the glass transition temperature for each pure substance is known. The interaction between polymer and plasticizer is not, however, taken into account. To obtain a better fit to the experimental data in this study, the following equation has been used:

$$T_g = T_{g1}w_1 + T_{g2}w_2 + Iw_1w_2$$

(3)

Equation 3 was introduced by Jenckel and Heusch [47] and has been successfully used by Chi and Lesikar to describe uncured and cured mixtures of polymers and energetic plasticizers [48] and organic solvent mixtures [49] respectively. I is an interaction parameter that relates to chain stiffness, free volume and molar cohesive energy [48], and it is thus a measure of the ability of the plasticizer to lower the glass transition temperature. If I is equal to zero, equation 3 describes a straight line in a T_g versus w_2 plot.

Figure 13 shows the experimental T_g (midpoint) data for the PolyNIMMO/NPN mixtures. An 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 of 3.3°C. A standard deviation of 3.3°C may seem large but, the maximum influence in equation 3 will be only 0.8°C when $w_1 = w_2 = 0.5$. The curve described by equation 3 is plotted in Figure 13 using the calculated interaction parameter. The linear correlation (I=0) and the Fox equation are used for comparison.
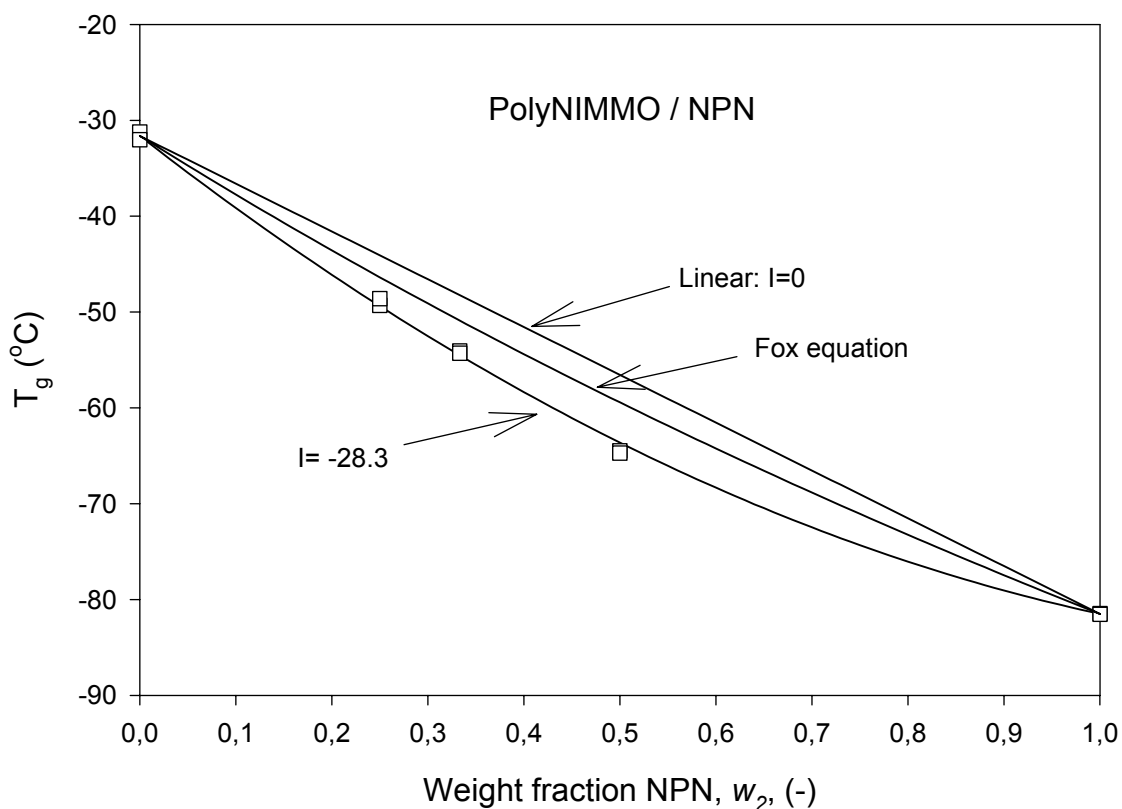
Figure 13. Glass transition temperature of uncured PolyNIMMO plasticized with NPN.

To compare the plasticizing effect of NPN in PolyNIMMO with that of other energetic plasticizers, the same procedure was repeated with butyl-NENA and BDNPA/F in combination with PolyNIMMO. The results are shown in Table 7 and Figure 14.

Table 7. Measured glass transition temperatures of the pure materials and of 50/50 PolyNIMMO/plasticizer mixtures and their calculated interaction parameters.

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.

The measured glass transition temperatures are in good agreement with literature data for pure PolyNIMMO (-30°C [34]), butyl-NENA (-84°C [32], -82.0°C [29]) and BDNPA/F (-65°C [32], -62.5°C [29]).
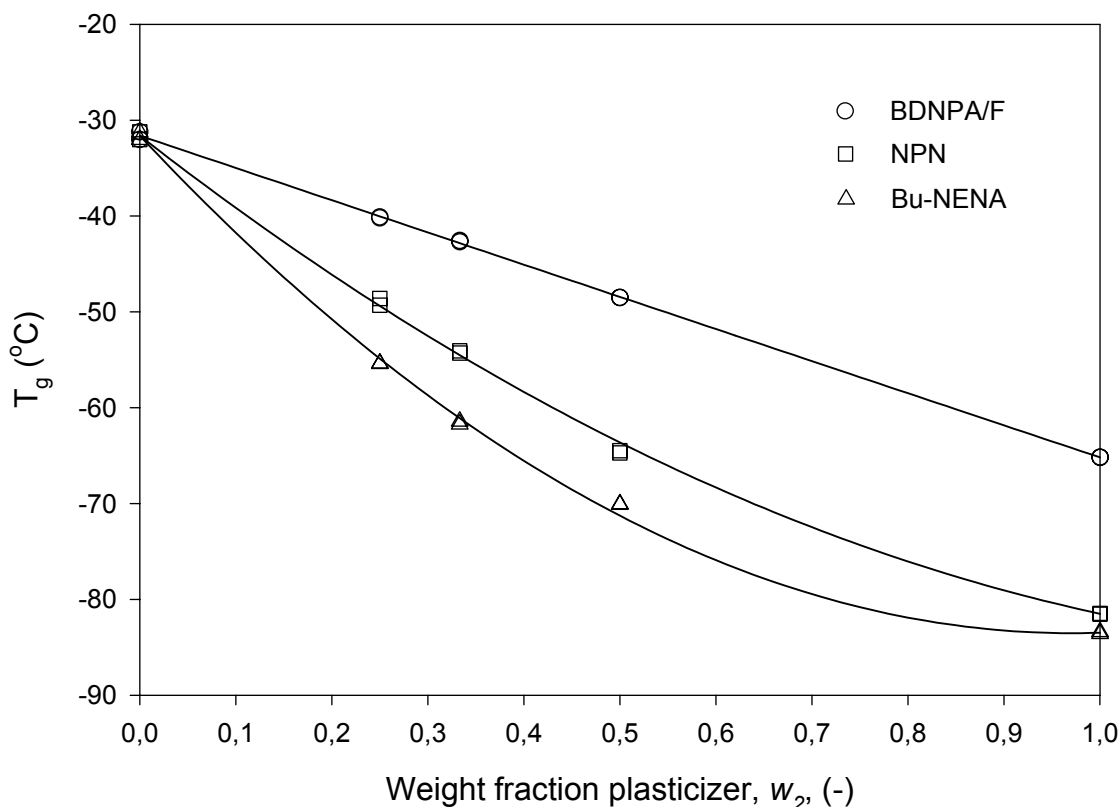

Figure 14. Glass transition temperature of uncured PolyNIMMO with different plasticizers.

The glass transition temperature of the PolyNIMMO/BDNPA/F-mixtures varied linearly with the plasticizer content (I=-0.1°C) and it thus seems that the glass transition depression is due only to dilution of PolyNIMMO. On the other hand, NPN and butyl-NENA, interacted strongly with PolyNIMMO (I= -28.3°C and -54.9°C respectively) and the glass transition was depressed to a substantially lower degree. The glass transition temperatures of NPN and butyl-NENA are similar but the very low interaction parameter for butyl-NENA made it much more effective. To obtain a glass transition of -50°C for uncured PolyNIMMO, the addition of 19% butyl-NENA, 26% NPN or 55% BDNPA/F is necessary, but increasing the amount of plasticizer decreases the tensile strength. At concentrations above 50%, the strength will probably be very low and it thus seems that BDNPA/F is not well suited as a plasticizer for PolyNIMMO.

When large amounts of plasticizers are mixed into a polymer, phase separation may occur [50]. 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, a much smaller depression of the glass transition temperature than expected can sometimes be observed, followed by an increase in the modulus at temperatures below the glass transition. This phenomenon is referred to as anti-plasticization [45,51]. In neither of these two cases will equation 3 correctly describe the glass transition temperature of the mixture. In this work, the validity of equation 3 at high (>50%) or low (<25%) levels of plasticizers in PolyNIMMO was not studied, since the main interested is in the intermediate range.

To improve the mixing and casting of composite propellants, a low viscosity of the uncured propellant is desired. Thus the ability of the plasticizer to lower the viscosity of the pre-polymer was measured on 50/50 mixtures of PolyNIMMO and plasticizer. It was found that NPN was almost equally as effective in lowering the viscosity of PolyNIMMO as butyl-NENA, Table 8, and this is considered to be very effective in this respect [29]. Literature data for HTPB are included for comparison.

Table 8. The viscosity of uncured 50/50 mixtures of PolyNIMMO and different plasticizers at 30 and 60°C. Measured at a constant shear rate of 1.0 s^{-1}.

Polymer	Plasticizer	Viscosity (Pa·s) at:	
		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
HTPB (R-45 HT)	-----	5.0^a, 5.4^b	

a) Data from reference [24].

b) Data from reference [52].

It is interesting to note that the influence of each plasticizer on lowering the viscosity follows the same trend as lowering the glass transition temperature. This is perhaps not surprising, since both physical processes will be favored by the plasticizer that increases the molecular mobility the most.

5. Conclusions

The tensile strength of HTPB-based polyurethane can be increased by a factor of almost ten by increasing the content of hard segments. Among the materials tested in this study, the highest tensile strength was obtained using H_{12}MDI and BDO. Improving the tensile strength by this method will not decrease the ultimate elongation and it will not alter the glass transition temperature to any great extent. This method thus seems very attractive for use in binders for propellants, where a large ultimate elongation and a low glass transition temperature are required. Other studies have shown that the tensile strength of HTPB can be further increased by using more bulky chain extenders and MDI [26,27]. This will, however, strongly decrease the ultimate elongation. The high melting point of the more bulky chain extenders will also make the processing more complicated. Without any chain extender, HTPB cured with IPDI or H_{12}MDI gave materials with the same mechanical properties.

PolyNIMMO is effectively plasticized by butyl-NENA or NPN. BDNPA/F was not however effective in this respect. NPN, which is the most energetic of the plasticizers studied, is thus very attractive as a plasticizer for PolyNIMMO. The influence of the plasticizer on lowering the viscosity follows the same trend as on lowering the glass transition temperature. This is probably because both physical processes are favored by the plasticizer which increases the molecular mobility the most.

6. Suggestions for future work

This work has shown that the tensile strength of HTPB-based polyurethane binder can be increased by a factor of almost ten without decreasing the ultimate elongation. It is not however known how, in the end, this will alter the mechanical properties of an AP/HTPB-based propellant. Increasing the hard segment content may also influence the burning rate, the density and the specific impulse. It would thus be interesting to manufacture an AP propellant with a binder based on HTPB, H_{12}MDI and BDO, and to examine its properties and compare them with those of a traditional AP/HTPB-propellant.

When new energetic materials such as the plasticizer NPN are studied, it is necessary to keep in mind properties such as its sensitivity and thermal stability. NPN is very attractive as an energetic plasticizer due to its good ability to lower the glass transition of PolyNIMMO and due to its high oxygen balance. A drawback of NPN is however its poor thermal stability. Attempts to stabilize NPN with conventional nitrocellulose/nitroglycerine stabilizers have been made, but none of these substances was able to stabilize NPN for more than 2 to 4 days at 65°C [53]. Further work should thus be focused on finding a suitable stabilizer for NPN or on synthesizing new energetic plasticizers with greater stability.

7. Acknowledgements

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