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Report title

Energetic thermoplastic elastomers as binder in solid propellants

Abstract (not more than 200 words)

ADN is a very desirable oxidiser with respect to energy and environmental aspects, but it is also known to decompose in the presence of common binder ingredients. In order to develop alternative binders, different thermoplastic elastomers have been synthesised. Successful attempts were made to produce copolymers of polyNIMMO with poly(ethylene-*co*-1,2-butylene)diol and pentanediol respectively. The cured materials had glass transition temperatures between -11°C to -16°C. The plates made of polyNIMMO-poly(ethylene-*co*-1,2-butylene)diol also had a melting peak between 50°C - 80°C. The T_g for the co-polymers is too high to match the service temperature requirements of -40°C to +60°C. Also, the mixtures solidify when removed from the heat source, making them difficult to work with. Since these copolymers are too difficult to melt process at temperatures below 90°C, they are for the moment not suitable for ADN-based propellants. A series of polyNIMMO-polyTMPO *block*-copolymers were made and also melt blends of polyNIMMO and polyTMPO were formed. The polyNIMMO-content in the copolymers was not more than 20mol% and the energy content compared to pure polyNIMMO was low. The copolymers showed to have acceptable elastic properties in the service temperature interval, while blends did not. However, small, exothermal phase transitions were discovered in the copolymers in the temperature interval of -15 - +5ºC, which could cause problems in ADN-matrix applications. A GAP-polyTMPO-copolymerization was also performed, but it was not successful.

Keywords

Ammonium dinitramide, ADN, thermoplastic elastomers, hyperbranched polyoxetane, copolymers, blends, curing, polymerisation

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Rapportens titel (i översättning)
Energetiska termoplastiska elastomerer som bindemedel i krut

Sammanfattning (högst 200 ord)

ADN är en mycket attraktiv oxidator ur energi- och miljöperspektiv, men är även känd för att brytas ned i närvaro av vanliga bindemedelsingredienser. För att eventuellt finna alternativa bindemedel har olika termoplastiska elastomerer syntetiserats. Lyckade försök att framställa sampolymerer mellan polyNIMMO och poly(etylen-*co*-1,2-butylen)diol respektive pentandiol har gjorts. De härdade materialen hade glastransitionstemperaturer på -11°C till -16°C. Plattorna med polyNIMMO- poly(etylen-*co*-1,2-butylen)diol hade även en smältpunkt mellan 50°C - 80°C. T_g hos sampolymererna är för höga för att möta servicetemperaturkraven på -40°C till +60°C. Blandningarna stelnar också när de avlägsnas från värmekällan vilket gör dem svåra att jobba med. Dessa sampolymerer är för tillfället ej lämpliga i ADN-baserade krut eftersom de är för svåra att smältprocessa vid temperaturer under 90°C. En serie polyNIMMO-polyTMPO *block*-sampolymerer har framställts och även smältblandningar av polyNIMMO och polyTMPO har tillverkats. PolyNIMMO-innehållet i sampolymererna var inte mer än 20 mol% och energiinnehållet jämfört med ren polyNIMMO var lågt. Sampolymererna visade sig ha acceptabla elastiska egenskaper i servicetemperaturområdet, vilket blandningarna inte hade. Dock upptäcktes små exoterma fasomvandlingar i sampolymererna i temperaturintervallet -15 - +5ºC, vilka skulle kunna utgöra problem i matrisapplikationer med ADN. En GAP-polyTMPO-sampolymerisation genomfördes också men utfallet blev ej lyckat.

Nyckelord

Ammonium dinitramid, ADN, termoplastiska elastomerer, hyperförgrenade polyoxetaner, sampolymerer, blandningar, härdning, polymerisation

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Utökad sammanfattning

Det har blivit allt viktigare med hög prestanda och miljövänlighet när det gäller utveckling av krut. Krutet som används i exempelvis startmotorerna till sjömålsroboten RB 15 består till största delen av ammoniumperklorat (AP) i en elastisk matris baserad på polybutadien. Denna typ av krut producerar stora mängder saltsyra vid förbränning. Saltsyra är både frätande och skadligt för miljön. Dessutom bidrar saltsyran till att det bildas stora mängder rök och det är t.ex. inte önskvärt hos taktiska missiltillämpningar. Ett sätt att lösa dessa problem är att byta ut AP mot ammonuimdinitramid (ADN). ADN är en mycket intressant oxidator i krut. ADN ökar prestanda både när det gäller impuls och brinnhastighet. Det innehåller inget klor och därför bildas minimalt eller ingen rök vid förbränningen. Eftersom det inte bildas klor eller andra giftiga ämnen vid förbränningen är ADN ett mycket miljövänligt alternativ till AP.

En av den vanligaste kruttypen idag är kompositkrut. Kompositkrut tillverkas genom att fysiskt blanda oxidator (i pulverform) med flytande bindemedel. Bindemedlet består av polymer, tvärbindare (även kallad härdare) och tillsatser som t.ex. mjukgörare, aluminium och brinnmodifikatorer. Blandningen värms sedan vid temperaturer på ca 50-70°C i upp till en vecka och under denna uppvärmning reagerar polymeren och härdaren kemiskt med varandra och bildar en elastisk gummimatris. Det är viktigt att bindemedlet är elastiskt så att krutet inte spricker vid mekaniska påfrestningar, som vid avfyring. Det är också viktigt att bindemedlet bibehåller sin elasticitet även vid låga temperaturer. I Sverige är kraven på krut att de ska vara elastiska och ha bra mekaniska egenskaper inom temperaturintervallet -40° till +60°C.

Ett problem med ADN är att det reagerar med de härdare som används i dagens krut. Detta är oacceptabelt då krutets stabilitet och mekaniska egenskaper påverkas negativt. För att undvika oönskade reaktioner mellan ADN och härdare behöver man ett bindemedel som inte kräver härdare. En termoplastisk elastomer (TPE) är ett exempel på ett sådant bindemedel. TPE:er har, liksom vanliga gummimaterial, elastiska egenskaper. TPE:er är inte kemiskt tvärbundna utan har istället fysikaliska tvärbindningar som gör att de kan smältas och lösas upp i vanliga lösningsmedel.

Detta gör att inga härdare behövs och på så sätt kan man undvika problemet med ADN. En annan fördel med TPE:er är att de vid behov kan återvinnas genom att smälta eller lösa upp krutet.

Denna rapport beskriver syntes av energetiska TPE:er (ETPE). Dessa innehåller en energetisk polymer, polyNIMMO, vilket ökar energiinnehållet i bindemedlet. Genom att använda en ETPE som bindemedel kan man minska halten oxidator men ändå få bibehållen prestanda. Lägre halt oxidator eller fyllmedel ger bättre mekaniska egenskaper hos krutet. Två typer av ETPE har syntetiserats. Den ena består av polyNIMMO och olika typer av dioler. Den andra är en sampolymer mellan polyNIMMO och en hyperförgrenad polyoxetan, polyTMPO.

Sampolymeren mellan polyNIMMO/poly(etylen-*co*-1,2-butylen)diol uppvisar lovande egenskaper. Den går att bearbeta genom uppvärmning och den gelar i närvaro av organiska lösningsmedel. Troligen skulle den kunna bearbetas i samma typ av utrustning som används vid tillverkning av nitrocellulosakrut. ETPE:n som består av polyNIMMO och hyperförgrenad polyTMPO uppvisar också lovande egenskaper. Den är t.ex. fullständigt kompatibel med ADN. Alla ETPE:er beskrivna i detta arbete behöver mjukgörare eftersom de för tillfället har för höga glasomvandlingstemperaturer (bör vara lägre än -40°C) de kräver även ytterligare modifiering för att kunna användas tillsammans med ADN i krutformuleringar.

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1. Introduction

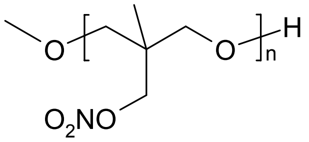
Over the years, high performance, insensitive munitions and pollution prevention issues in relation to solid rocket propellants have grown in importance. Solid rocket propellants traditionally used by e.g. the space launcher are based primarily on ammonium perchlorate (AP) dispersed in a polybutadiene (HTPB) binder. Such propellants can produce a significant amount of hydrogen chloride, a corrosive and toxic gas that contributes to the formation of secondary smoke under certain atmospheric conditions, and that is undesirable for certain applications. Furthermore, current minimum-smoke propellants contain large quantities of nitramine explosive that makes them detonable in tactical missile configurations. One approach to solve this problem is to replace the AP with a chlorine-free oxidiser, such as ammonium dinitramide (ADN). ADN is a very desirable oxidiser with respect to energy and environmental aspects, but it is also known to decompose in the presence of common binder ingredients, such as isocyanates.

Thermoplastic elastomers, TPE:s, offer an interesting choice as an alternative binder material in explosives and propellants. Basically, thermoplastic elastomers are copolymers of ABA or AB type, where A and B are hard and soft segments respectively. The hard segment is capable of crystallisation or association leading to thermoplastic behaviour, whereas the soft segment provides elastomeric characteristics to the copolymer. At temperatures above the softening point of the hard blocks, the chains are separated which makes it possible to process the TPE, for example by extrusion. When cooling the material it regains its properties resembling that of a cured rubber material. Since there are no chemical bonds between the molecular chains, the material is reprocessable. With no need for curing the material, the problem with incompatibility between ADN and isocyanates is avoided.

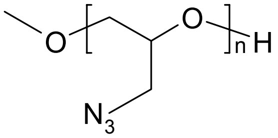
One problem with traditional TPE:s is that their molecular weight is very high and they soften rather than melt, which leads to high viscosity processing problems. Traditional TPE:s also have the undesirable property of high softening points. Therefore, it would be desirable with a TPE that have lower viscosity in the melt and a lower softening point. Also, traditional thermoplastic elastomers are non-energetic, so to be able to obtain even more energy from the propellant, an energetic binder would be preferable. Energetic Thermoplastic Elastomers (ETPE) are simply thermoplastic elastomers with an energetic content. The energetic content is exerted by an energetic polymer in the TPE backbone structure. Two examples of energetic polymers are polyNIMMO (Poly-(3-nitratomethyl-3-ethyloxetane) and GAP (Glycidyl Azide Polymer), which are illustrated in Figure 1. These two energetic polymers have shown to be compatible with ADN (Figure 1) in earlier work performed at FOI and DSTL [1].

$NH_4^+ \ N(NO_2)_2^-$

Ammonium Dinitramide (ADN)



Poly(NIMMO)



Glycidyl Azide Polymer (GAP)

Figure 1. *Energetic constituents in possible ETPE formulations. Molecular structures of the oxidiser ADN and two energetic polyethers, polyNIMMO and GAP (difunctional, hydroxy-functionalised), are illustrated.*

The same basic requirements for the ETPE-based matrix apply, as for the chemically crosslinked propellant formulation. While compatibility with ADN is the most fundamental requirement, several other crucial aspects have to be fulfilled:

- The matrix should exhibit elastic properties at -40°C − +60°C
- The formulation should be processible below 92°C (melting point of ADN)
- The matrix should not exhibit major phase transitions in the temperature interval specified.

A few energetic thermoplastic elastomers have been developed, such as a copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis-azido methyloxetane) (AMMO/BAMO)[2] and copolymers of poly(glycidyl azide) and poly(α-azidomethyl-α-methyl-β-propiolactone) [3] or poly(3,3-bis-azido methyloxetane) [4].

Two different types of energetic thermoplastic elastomers have been made at FOI. One is a copolymer consisting of polyNIMMO with different diols, connected with an isocyanate, and the other is a copolymer of polyNIMMO and a hyperbranched polyoxetane.

1.2 PolyNIMMO-diol copolymers

The aim with the experiments was to produce ETPE:s where the elastic block is made of polyNIMMO, connected to hard blocks consisting of an diol and an isocyanate. The desired molecular shape is to have polyNIMMO (soft block) in the middle with a diol (hard block) on each side. The urethane groups formed, when reacting a hydroxyl group with an isocyanate group, are capable of forming hydrogen bonds with e.g. another urethane group. By doing so, physical cross-links are obtained between the molecular chains. Isocyanates with aromatic rings have a great tendency to align, assembling the urethane groups, promoting hydrogen bond formation. The mechanical properties of the copolymers are directly related to the number of hydrogen bonds formed. A high degree of alignment will result in the formation of a high number of hydrogen bonds. This gives strong hard segment domains and therefore, strong copolyurethane thermoplastic elastomers.

1.3 PolyNIMMO-hyperbranched polyoxetane

A diploma work has previously been done on developing a polymer matrix for ADN-based propellants [5]. In a subsequent diploma work at FOI and KTH a continued work on this subject has been made. The aims of this work were several:

- To form an energetic thermoplastic elastomer (ETPE) containing polyNIMMO, a commercially available energetic polymer, and polyTMPO (Poly-(3-hydroxy-3-ethyloxetane)) a hyperbranched polyoxetane, shown to be compatible with ADN [5].
- To monitor slow versus instant addition of monomer in the copolymerisation reactions in order to determine if the propagation mechanism differ during the reaction, thereby affecting the polyNIMMO content in the products

- To form blends of polyNIMMO and polyTMPO in the same compositions as the copolymer products in order to make a comparison of thermal and mechanical properties
- To increase the polyNIMMO content in the copolymer products to achieve a higher energetic content in the ETPE
- To evaluate another energetic TPE system, GAP-*co*-polyTMPO, based on the experiences from the polyNIMMO-polyTMPO experiments

Thermoplastic elastomers are characterized by having both stiff and soft segments in their backbone structure. In the ETPE produced in this work, the soft segment is the energetic polymer (polyNIMMO or GAP) and the stiff segment is the hyperbranched polymer of TMPO (Figure 2). Earlier work has shown that polyTMPO is compatible with ADN [5].

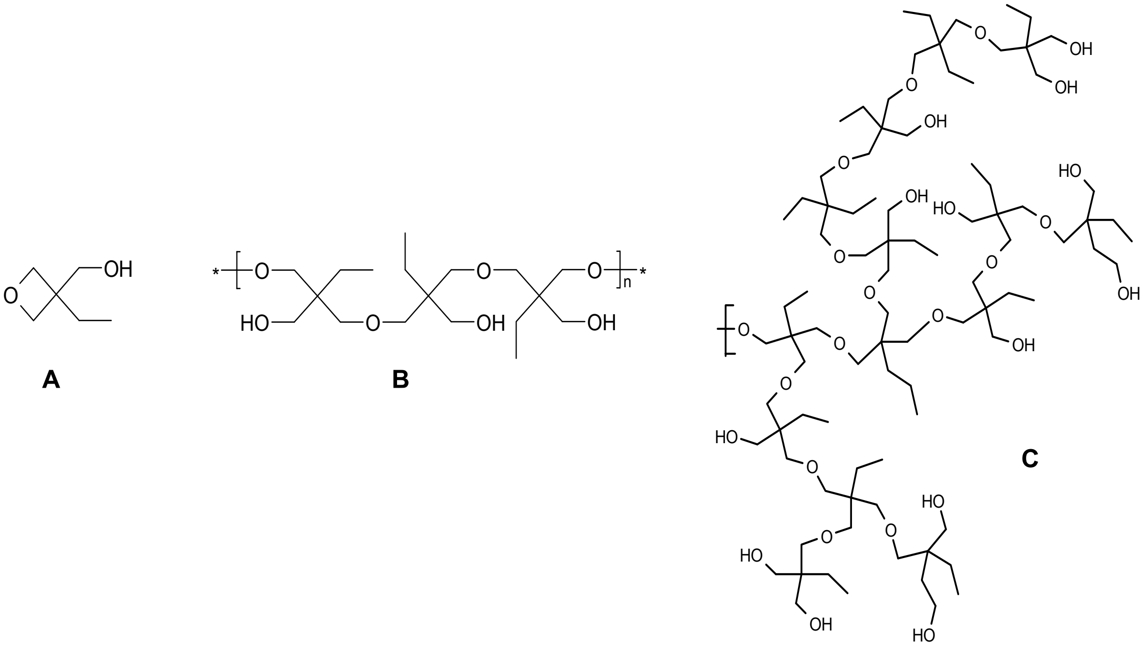


Figure 2. *Structure of TMPO in the monomer form (A), the linear polymer form (B) and the hyperbranched polymer form (C).*

Description of hyperbranched polymers and their properties compared to the linear counterpart is given by Kakimoto [6].

The elastic nature of the binder matrix is formed by entanglement between the hyperbranched units of the copolymers. Crystallisation and hydrogen bonding between the hydroxy-groups of the TPE units will further improve the strength of the physical crosslinks in the formed matrix.

The polymerisation of ring-strained polyoxetanes, such as TMPO, propagates through cationic ring opening polymerisation (CROP). Two different propagation mechanisms are present: activated chain end mechanism (ACE) and activated monomer mechanism (AM). These mechanisms are thoroughly described elsewhere [5]. The ACE mechanism leads to formation of a linear polyoxetane polymer, while an AM mechanism solely leads to a branched structure. When both mechanisms are present, a hyperbranched polyoxetane is formed [7]. The ACE mechanism is preferred when monomer conversion is low, while the AM dominates when monomer conversion is high. Evidence of these phenomena has been shown in the work of Penczek et al [8].

The idea of forming an energetic thermoplastic elastomer based on a four-membered, ring-strained oxetane and polyNIMMO is based on the principle that the polyNIMMO hydroxyl end groups will act as nucleophiles in an AM mechanism. The end group attaches to TMPO, which ring-opens, resulting in a new nucleophilic hydroxyl end group. The propagation will then result in a hyperbranched ETPE (Figure 3).

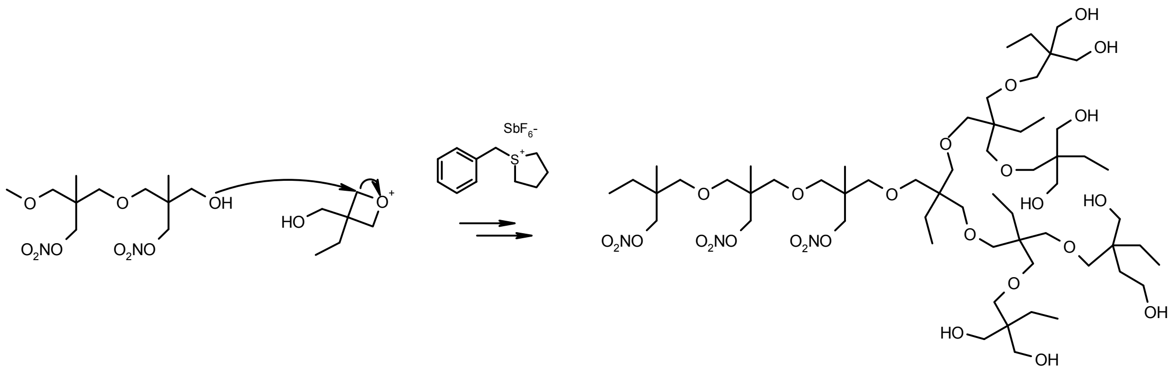


Figure 3. *Formation of a polyNIMMO-polyTMPO energetic TPE by an activated monomer mechanism (AM). The initiator- Benzoyl Tetrasulfonium Hexafluoroantimonate (BTSSbF$_6$) is also shown.*

2. Experimental

2.1 Materials

PolyNIMMO, Poly(3-nitratomethyl-3-methyloxetane), difunctional, (Nobel Enterprices, UK); Poly(1,4-butyleneadipate)diol, (Aldrich, Sweden); Poly(ethylene-co-1,2-butylene)diol, (Aldrich, Sweden); Polycaprolactonediol, (Aldrich, Sweden); 2,4-Pentanediol, (Aldrich, Sweden); DBTDL, dibutyl tin dilaurate, (Merck, Germany); H_{12}MDI (Desmodur W), dicyclohexylemethane-4,4´-diisocyanate, (Bayer, Germany); MDI, 4´,4´-methylenebis(phenyl isocyanat) , (Aldrich, Sweden); TMPO, 3-hydroxy-3-ethyloxetane, (Perstorp Polyols Inc., Sweden); PolyTMPO, Poly-(3-hydroxy-3-ethyloxetane), (Prepared according to literature procedures [9]); GAP, poly(glycidyl azide), (SNPE, France); $BTSSbF_6$, benzoyl tetrasulfonium hexafluoro antimonate, (Manufactured according to literature procedures [10]); BF_3OEt_2, boron trifluoride etherate, (Lancaster Synthesis Ltd., UK).

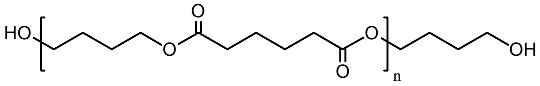
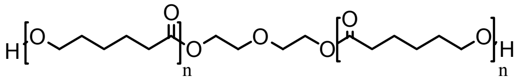
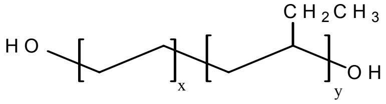
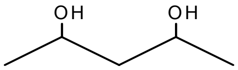
2.2 Methods

2.2.1 Synthesis

2.2.1.1 PolyNIMMO-diol-copolymers

Attempts have been made to produce different TPE:s where the elastic block is made of polyNIMMO, connected to hard blocks consisting of an diol and an isocyanate. Four different diols has been used as the hard block; poly(1,4-butyleneadipate)diol, polycaprolactonediol, poly(ethylene-*co*-1,2-butylene)diol and pentanediol (Table 1).

Table 1. *Different diols used in synthesis of TPE:s.*

Substance	**Structure**	**Molecular weight**	**Melting temperature (°C)**
(1,4-butylene-adipate)diol		1000	50-60°C
polycaprolactonediol		2000	~60°C
poly(ethylene-*co*-1,2-butylene)diol		2500	60-80°C
pentanediol		104	--

Two different isocyanates have been used to connect the diol with polyNIMMO; H_{12}MDI (dicyclohexylemethane-4,4´-diisocyanate) or MDI (4´,4´-methylenebis(phenyl isocyanat)). The amount of diisocyanate, m_{NCO}, required in the reaction was calculated according to the following equation;

$$\frac{f_{NCO}}{M_{NCO}} \cdot m_{NCO} = \left(\frac{HOV_{polymer}}{56100} \cdot m_{poklymer} + \frac{f_{OH}}{M_{OH}} \right) \cdot \left(\frac{NCO}{OH} \right) \qquad (1)$$

where *f* is the functionality, *M* is the molecular weight, *m* is the amount of the compound in question and subscript *OH* and *NCO* is for the diol and isocyanate, respectively. The $\left(\frac{NCO}{OH} \right)$ ratio has been one in all experiments and the molar ratio between the diol and polyNIMMO has been kept at 2:1. The reaction between the hydroxyl groups of the diol and polyNIMMO with the isocyanate was done in the same way in all the experiments. Stirring of the mixture was made by hand with the beaker down in an oil bath while heating. After melting the diol, polyNIMMO was added and the two were thoroughly mixed. The isocyanate and DBTDL were added at the end. The samples were degassed to avoid blisters in the product, and finally the mixture was poured between two plates and left to react at 60°C.

2.2.1.2. PolyNIMMO-hyperbranched polyoxetane

A series of polymerisations were performed, both in bulk and in solution, in order to form a polyNIMMO-polyTMPO copolymer. Polymer blends with the same composition as the copolymer products were prepared to compare thermal and mechanical properties of the different formulations. The polyTMPO needed for the blends was synthesised according to literature procedures [9].

Several bulk polymerisations were performed, using TMPO and polyNIMMO in equivalent weight ratios for most polymerisations. TMPO monomer was added during 1.0-1.5 hours in the slow addition reactions. $BTSSbF_6$ (0.4wt%, relative to TMPO) and BF_3OEt_2 (0.4mol%, relative to TMPO) were used as initiators and the reaction temperature varied from 100-120°C. Reaction time was approximately 4-5 hours and monomer conversion reached 75-80%. The results from the bulk polymerisations are shown in Table 4, Appendix 1.

Polymer blends were prepared by melt mixing at 130-140°C, well above the T_g of TMPO and polyNIMMO, to attain an acceptable viscosity of the mixture. This procedure was selected to avoid problems encountered earlier with discarding remaining solvent in solution blending procedures [5]. Two blends with 10 mol% and one blend with 20mol% polyNIMMO were prepared. The blending was performed by mechanical mixing with an RW20 IKA stirring motor for approximately 4-5 hours at 130-140°C. Results from the melt blending experiments are shown in Table 5, Appendix 1.

Solubility tests were performed to determine suitable solvents for use in solution polymerisation experiments. Tetrahydrofurane (THF), chloroform ($CHCl_3$) and toluene were found to be the most suitable solvents. The solubility tests are summarised in Table 7, Appendix 2. Ethyl acetate (EtOAc) showed a selective solubility towards polyNIMMO, which was used to separate unreacted polyNIMMO and TMPO monomer from copolymer products. The selective solubility was a confirmation of earlier work performed by Borong et al [5]. Another important feature discovered was that 1-butanol and 2-propanol showed selective solubility towards polyTMPO, which could be used in future experiments for separation of unreacted polyTMPO from polyNIMMO-polyTMPO copolymer.

To increase the polyNIMMO content in the copolymer products, a series of solution polymerisations were performed, using the different solvents chosen from the solubility tests described earlier. All experiments were performed under an argon atmosphere (99.996%, AGA Gas AB) at temperatures of 0-100°C, depending on solvent. The reaction time varied from 4-24 hours. All reactions were quenched with ethanol (99.5%, Kemetyl AB) to deactivate the initiator. BF_3OEt_2 (1.0mol%, relative to TMPO) was used as initiator. The results of the solution polymerisations are summarised in Table 6, Appendix 1.

A solution polymerisation of GAP-polyTMPO was performed, based on earlier experiments made with polyNIMMO as energetic polymer. The experiment was performed in $CHCl_3$ at 55°C, under an argon atmosphere. GAP and TMPO were used at a 1:1 weight ratio, with a total weight of 1.0g. $BTSSbF_6$ was used as initiator (0.4 wt% with aspect to TMPO). The reaction was quenched with EtOH (1mL) after 5 hours.

2.2.2 Analytical methods

The reaction progress in the polymerisation reactions was monitored by ^{1}H-NMR continuously during the reactions, using a Bruker 1D FT-NMR 400MHz. Dimethyl Sulfoxide (DMSO-d_6, 99,5% Aldrich) was used as NMR-solvent and internal standard.

All samples analysed, blends and copolymer products, were dried under vacuum for at least three days before analysis.

The polyNIMMO-content was analysed by ^{1}H-NMR (as mentioned above) and IR.

IR analysis was performed by using a Perkin Elmer Instruments Spectrum GX Raman FT-IR Spectrometer Spectrum 2000R, with a Graseby Specac Golden Gate Single Reflection Diamond ATR. A minimum of two runs per sample was performed and a mean value was calculated.

The polyNIMMO-content was determined by calculating the absorbance areas for the characteristic peaks of the nitrato asymmetric and symmetric stretch of polyNIMMO, further depicted in section 3.2.1.2., Figure 6, before and after wash of the products. However, the attenuated total reflectance (ATR) method poses limitations to the comparison of absorbance peaks in different IR-spectra, due to reflection phenomena in the diamond crystal used, and therefore an internal reference peak close to the characteristic polyNIMMO peaks was chosen to be able to correlate the IR-results.

Molecular weight analysis was performed by size exclusion chromatography (SEC), using a Waters 6000 pump, with a PL-EDM 960 light scattering detector, a Waters temperature control module and a Waters 717 autosampler. Dimethyl formamide DMF (99.6%, Lancaster), was used as solvent and linear polyethylene glycol (M_{peak} from 100-125000g/mol, PDI from 1.00-1.05) was used as standard.

Density was measured using a Micromeritics 1330 Accupyc pycnometer. Helium (99,996%, AGA Gas AB) was used as purging gas. Measurements were performed at a temperature of 25-26°C and at a relative humidity of 30-35%.

Elemental analysis (EA) was performed by Kolbe Mikroanalytisches Laboratorium, Germany.

Calorimetric measurements were performed by using an IKA-Calorimeter System C4000A Adiabatic. Benzoic acid ($\Delta H_c = -26458 \pm 20$ J/g, IKA Labortechnik) was used as standard substance.

Water content analysis were made by an Orion AF8 volumetric Karl Fischer titrator, using water-free methanol (<0,005% H_2O, Riedel-de Haën) as media and Hydranal Composite 2 as reagent. A series of three runs per sample were made and a mean value was calculated.

Mechanical properties were analysed using a Reologica StressTech Melt HR rheometer. The measurements were done at a relative humidity (RH) of 30-35%. All samples were heated for 15 minutes at 120°C to lower the viscosity of the material to get an acceptable surface adhesion. A standard flat aluminium bottom plate and a 20mm (diameter) flat aluminium top plate were used. The gap between the plates was 1.00 mm. An oscillation stress sweep, from 100 to 10.000 N, was performed for all samples to determine the optimal applied stress during measurement. The mechanical properties were measured by a frequency sweep from 1 to 10 Hz at an applied stress of 3000 N. The frequency sweep measurements were performed at -40, 5, 25 and 60°C. Cooling media used was liquid nitrogen (99,5%, AGA Gas AB).

Differential scanning calorimetry, DSC, of the polyNIMMO-diol copolymers was performed on a Mettler DSC 30. Heating and cooling scans were performed at 10˚C/min and 40µL standard aluminum pans with perforated lids were used. All experiment were performed under inert nitrogen gas with a flow rate of 50 ml/minute. The glass transition temperature, T_g, was calculated according to equation 2.

$$T_g = \frac{T_{gOn} + T_{gEnd}}{2} \qquad (2)$$

Where the temperature at the onset, T_{gOn}, and the endset, T_{gEnd}, were taken as the intercept of the extrapolated tangents on the DSC-curve and determined on the second heating.

Thermal analysis on the polyNIMMO-hyperbranched polyoxetane was performed by Differential Scanning Calorimetry (DSC), using a Mettler Toledo DSC820. 20µL standard aluminium pans with perforated lids were used. A heating rate of 10°C/min, a cooling rate of -10°C/min and a nitrogen flow of 80mL/min (99,996%, AGA Gas AB) were used. Sample weights varied from 6-10mg. Same thermal history was used for all samples: the temperature curve starting at 25°C, cooling to -40°C, isothermal at -40°C for 1min, heating to 140°C, isothermal at 140°C for 1min, then cooling to -40°C. The data for all results was collected from the second cooling sequence. T_g was determined as the inflection point of the exothermic inclination in the thermogram.

The oxygen balance of the different polyNIMMO-hyperbranched polyoxetane copolymer products and blends was estimated by using EA- and SEC-data (M_n) to determine the molecular weight and the number of different atoms present in the macromolecule. The oxygen balance was calculated using the expression:

$$\Omega = \frac{[O - (2 \times C) - (H/2)] \times M_O}{M} \times 100 \qquad (3)$$

where: Ω = Oxygen balance (in percent)

O = Number of oxygen atoms in compound molecule

C = Number of coal atoms -"-

H = Number of hydrogen atoms -"-

M_O = Molecular weight of oxygen

M = Molecular weight of the compound

The compound has a general formula of $C_C H_H N_N O_O$, where the index denotes the number of atoms present in the molecule.

3. Results and Discussion

3.1 PolyNIMMO-diol copolymers

Several attempts to react polyNIMMO with poly(1,4-butyleneadipate)diol, PBA, or polycaprolactonediol, PCl, were made but none of them were successful. Both materials initially felt tough but broke on tension.

Mixing polyNIMMO with poly(ethylene-co-1,2-butylene)diol, PEB, resulted in a material which felt very strong and tough. DSC measurements on this material showed a melting peak between 50°C and 80°C, which is in accordance with the melting point for PEB. Attempts to melt the polymer in the reometer did not work, but the material softened substantially after been kept at 100°C for a while. This indicates that addition of the oxidiser can be made by mixing the material at an elevated temperature. Further investigations are however necessary before any conclusion can be made.

DSC measurements of the material gave a T_g value of -16°C. T_g for PEB alone is difficult to detect, but a probable value is -50°C. PolyNIMMO alone has a glass transition temperature of approximately -30°C, and curing the polymer makes the T_g approximately 10°C higher [11]. The T_g for the copolymer is too high to match the service temperature requirements of -40°C to +60°C. It would therefore be necessary to modify the structure, for example by altering the OH/NCO ratio and/or by using a different ratio between the diol and polyNIMMO. Also, the addition of plasticisers could be necessary.

Samples (in the shape of plates 12*12*2 mm) with polyNIMMO and 2,4-pentandiol have been made with two different isocyanates; H_{12}MDI and MDI. The plate with H_{12}MDI as isocyanate felt slightly more flexible (T_g of -13°C) than the one with MDI (T_g of -11°C). None of the two materials showed any melting below 180°C, which is the temperature at which polyNIMMO decomposes.

As soon as the mixtures are removed from the heat source they immediately solidify. This makes the degassing of the mixture impossible and because of that the TPE is full with blisters. There is also the problem of filling moulds before the material solidifies.

3.2. PolyNIMMO- hyperbranched polyoxetane

3.2.1. PolyNIMMO-polyTMPO copolymers and blends

3.2.1.1. Formation of a Copolymer

^{1}H-NMR showed presence of polyNIMMO in the polymerisation products after extensive wash with EtOAc, which strongly indicated formation of a copolymer. Stress sweeps performed by rheometer showed that the copolymers had a storage modulus of a factor 10 or more in magnitude compared to polyNIMMO-polyTMPO blends produced, which confirmed that a copolymer had been formed.

Reaction progress during the polymerisation reactions was observed continuously by ^{1}H-NMR, illustrated in Figure 4.

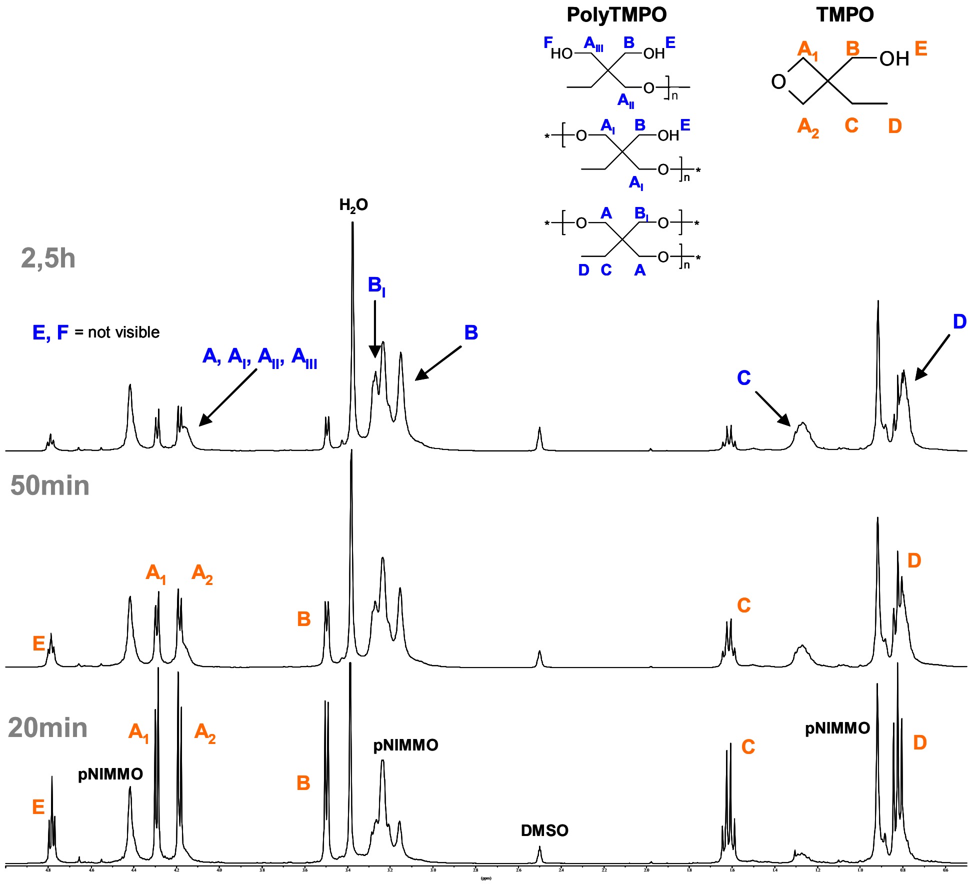


Figure 4. *Reaction progress monitored by ^{1}H-NMR during the polymerisation reaction. The spectra show a gradual decrease of monomer as the TMPO* co-*polymerises with polyNIMMO. The spectra illustrate slow addition of TMPO to polyNIMMO in bulk (experiment P9).*

3.2.1.2 PolyNIMMO content in Products

The polyNIMMO content in the copolymer products and blends were analysed by both ^{1}H-NMR, as illustrated in Figure 5, and FT-IR, depicted in Figure 6. The analyses were made before and after the wash of product with EtOAc, which was made to separate unreacted monomer and polyNIMMO.

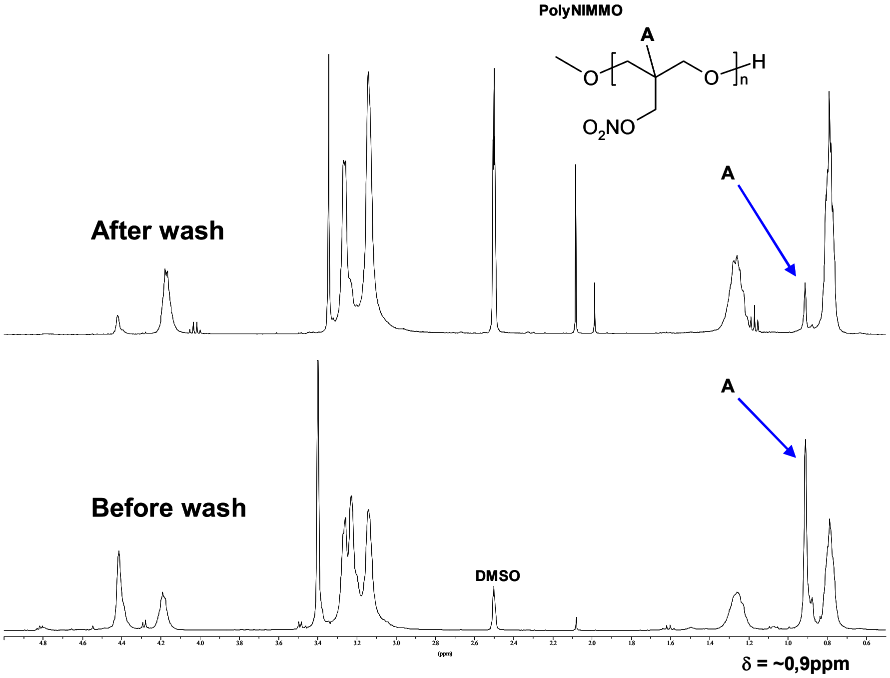


Figure 5. *Illustration of polyNIMMO-content determination using* ^{1}*H-NMR (experiment P25). The chemical shift of the polyNIMMO methyl group differed by 0.1ppm from the polyTMPO methyl group (*δ *= ~0.8ppm) and therefore was chosen for calculation of polyNIMMO-content in the copolymer products. The area of the methyl group was calculated before and after wash with EtOAc.*

The results from the ^{1}H-NMR and FT-IR differed in estimation of polyNIMMO content. IR seemed to overestimate the amount of polyNIMMO present in the copolymers, while NMR probably gave a more correct estimation of the amount of energetic polymer present in the ETPE:s. This assumption is based on the NMR-results from the blends (with known polyNIMMO content) produced, showed in Table 5, Appendix 1.

A correlation between the NMR and the IR results is given in Table 8, Appendix 3, and illustrates that IR show a polyNIMMO-content of up to almost 50mol%, while NMR show a content of up to 23mol%.

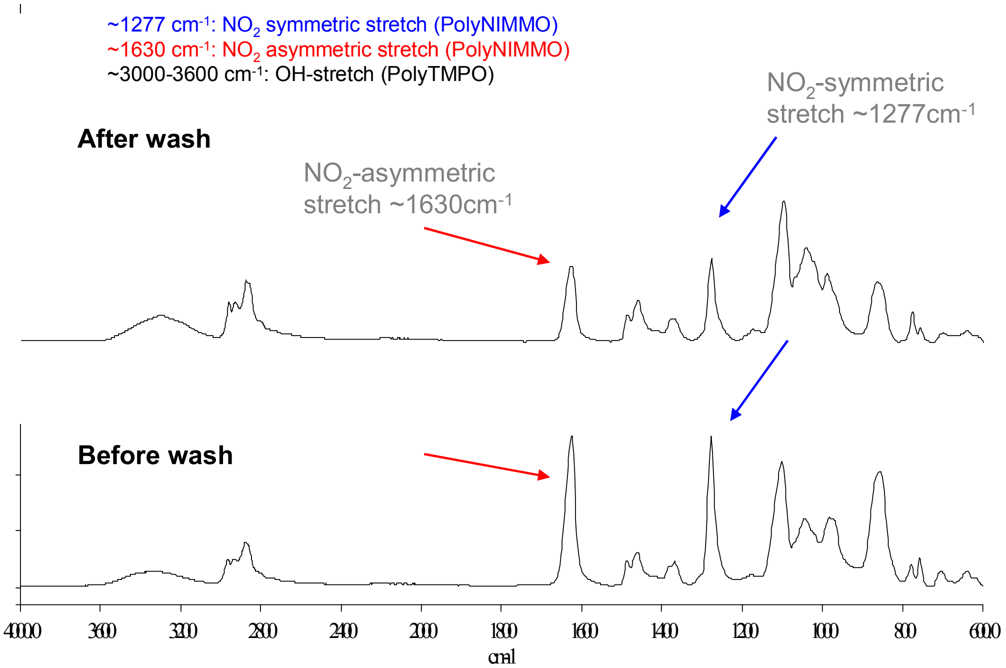


Figure 6. *IR-spectra from FT-IR ATR analysis made on samples before and after wash with EtOAc (experiment P9). The PolyNIMMO-content was determined by calculating the absorbance area for two separate characteristic peaks, illustrated by arrows. Presence of polyTMPO and possible unreacted TMPO are also seen in the spectra.*

Analysis performed by ^{1}H-NMR during the reactions showed that there was no significant difference in monomer conversion for slow versus instant addition of TMPO monomer, as illustrated in Figure 7. The monomer conversions reached 70-80%, the viscosity of the mixture then limited further reaction. The polyNIMMO-content was approximately the same for copolymers produced by either method, which was expected due to lack of domination of the AM mechanism described in 1.3.

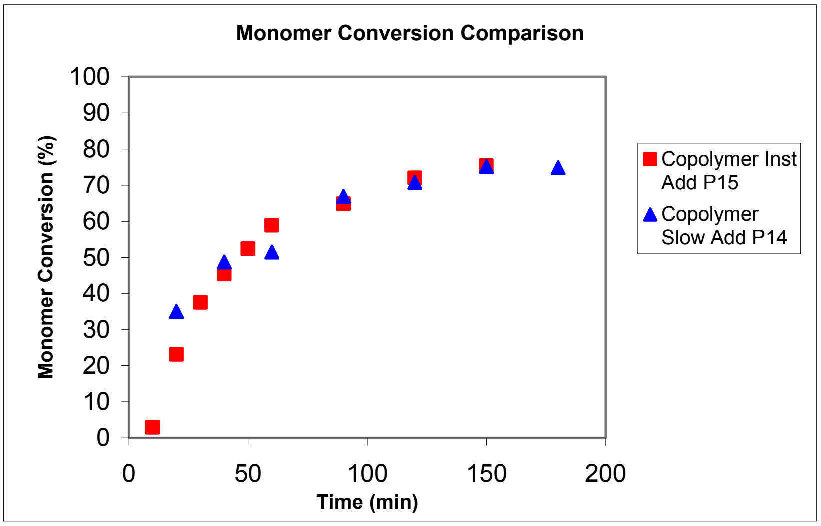


Figure 7. *Monomer conversion curves for instant versus slow addition of TMPO monomer. Analysis performed by* ^{1}*H-NMR (DMSO).*

For solution polymerisation products, the monomer conversion reached up to 98% in some cases, but the polyNIMMO-content did not increase.

3.2.1.3. Molecular Weight Analysis

The results from the molecular weight analysis showed that there was an increase in molecular weight for most bulk copolymer products compared to the M_n of polyNIMMO (1522 g/mol, analysis performed by SEC), and a molecular weight decrease for most solution polymerisation products. The results of the analyses are shown in Appendix 1, Table 4, 5, and 6, respectively. The molecular weight decrease can be explained by the existence of a high molecular weight fraction present in the samples analysed, which probably is from polar aggregates formed by the many polar hydroxyl end groups in polyTMPO.

The method used for molecular weight analysis (SEC) underestimates the molecular weight of the products containing hyperbranched polyTMPO, due to the use of linear standards when calibrating the system. Hyperbranched molecules have a smaller hydrodynamic volume than their linear analogues and therefore they stay in the column for longer periods of time, with the result of a longer retention time in the analysis, and thereby an underestimation of the molecular weight.

The formation of polar aggregates together with the underestimation of molecular weight by using SEC made it difficult to estimate the correct molecular weights of the copolymers and blends produced.

3.2.1.4. Physical Properties

Elemental analysis confirmed the results attained from polyNIMMO-content analysis performed by NMR. The polyNIMMO-content is represented by nitrogen for the different polymers, illustrated in Table 2.

Table 2. *Elemental analysis results*

Experiment	***C***	***H***	***N***	***O***
(#)	***(wt%)***	***(wt%)***	***(wt%)***	***(wt%)***
PolyNIMMO	41,52	6,48	9,39	42,40
PolyTMPO (P16)	61,79	9,92	0,0	28,41
Blend (P18)	59,33	9,81	0,98	29,65
Copolymer (P4)	57,86	9,80	1,35	30,74

Heat of formation for the copolymer product was calculated using molecular weight data from SEC analysis, polyNIMMO-content data from ^{1}H-NMR and elemental analysis results. Table 3 illustrates that the copolymer has a quite low energy content compared to the homopolymer of polyNIMMO.

Table 3. *Oxygen balance, density, heat of formation and water content results.*

Experiment	***Oxygen Balance***	***Density***^{1}	***ΔH_f***	***Water Content***
(#)	***(%)***	***(g/cm^3)***	***(kJ/kg)***	***(wt%)***
PolyNIMMO	-114	1,26	-2673 [12]	-
PolyTMPO (P16)	-215	1,11	-	0,40
Blend (P18)	-207	1,12	-	0,38
Copolymer (P4)	-202	1,10	-4144	0,31

^{1}*Density measurements made at a temperature of 25-26°C.*

The low water content in the copolymers was not a major factor in possible termination of the different polymerisation propagation reactions, a conclusion made from the results given in Table 3.

3.2.1.5. Thermal Properties

DSC results showed two distinct T_g:s for both copolymers and blends, illustrated in Figure 8 and 9. $T_{g,1}$ originates from the polyNIMMO-part ($T_{g,\ \mathrm{pNIMMO}}$ = -29ºC) of the copolymer and $T_{g,2}$ represents the polyTMPO-part ($T_{g,\ \mathrm{pTMPO}}$ = 40-55ºC).

$T_{g,1}$ for the different blends varied from -31 to -28ºC and $T_{g,2}$ varied from 32-35ºC. A suppression of the second T_g could be the result of homogenous parts in the phase separated blends.

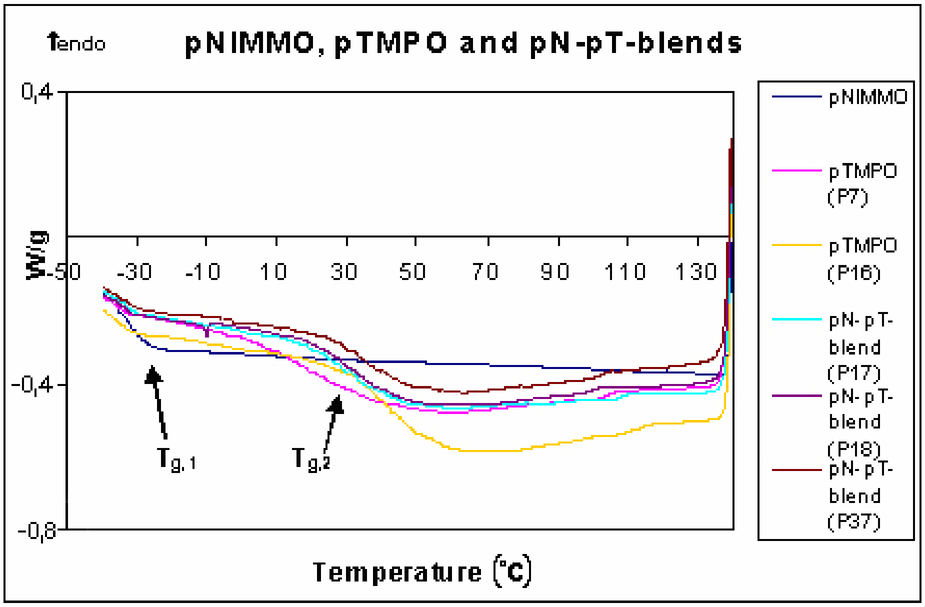


Figure 8. *DSC thermograms from the homopolymers of polyNIMMO and polyTMPO and the blends produced, showing two distinct* T_g*:s for the blends.*

For the copolymer products $T_{g,1}$ varied from -31 to -29 and $T_{g,2}$ from 34-51ºC. A higher second glass transition temperature compared to that of pure polyTMPO could be observed for the copolymer products. This increase could originate from linear low molecular weight segments crystallising in the copolymer. PolyNIMMO and polyTMPO in the copolymer products are phase-separated, which strongly suggests that a TPE structure has been formed.

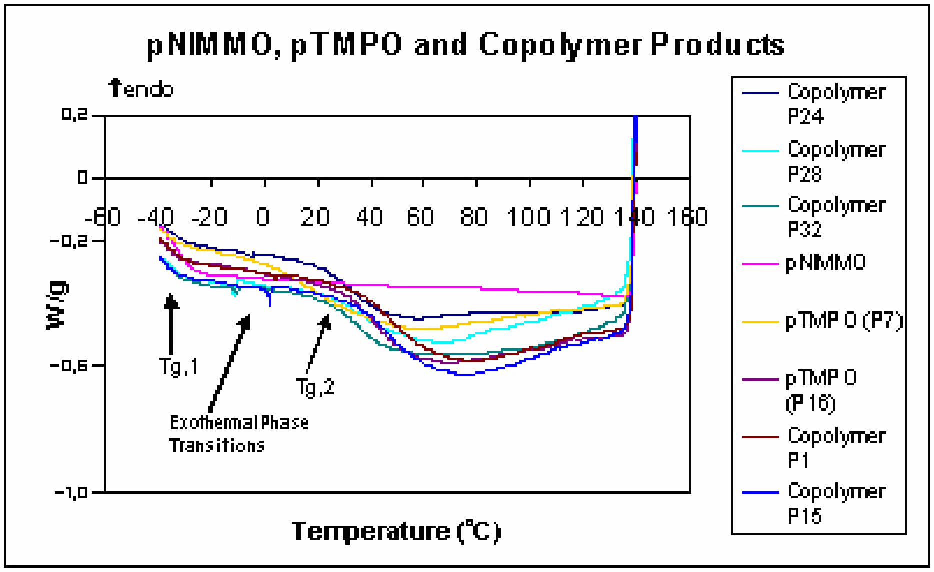


Figure 9. *DSC thermograms from pNIMMO, pTMPO and some of the copolymers produced, showing two T_g:s and a small exothermal phase transition for the copolymers.*

Exothermal phase transitions in the temperature interval of -15 to 5ºC were discovered in most of the copolymer products (Figure 9). The reason for these small transitions is probably crystallisation of linear low molecular weight segments in the copolymers.

3.2.1.6. Mechanical Properties

Rheology analysis showed that the storage modulus for the copolymers was higher with a factor 10 or more, compared to the blends prepared, at a temperature above both $T_{g,1}$ and $T_{g,2}$, as illustrated in Figure 10. There was also a great difference in mechanical properties between the different copolymer products analysed. At temperatures between $T_{g,1}$ and $T_{g,2}$ the mechanical properties of copolymers and blends were approximately the same, but at 5ºC crack formation was discovered in several copolymer samples, causing the material to release from the rheometer plates. The result is shown in Figure 10 as a total loss of storage modulus for the copolymers. At -40ºC, below both T_g:s of the blends and copolymers, there were difficulties in attaining relevant data for all samples analysed, as illustrated in Figure 10. Therefore, to be useful, the analysis method needs further evaluation for analysing samples at these low temperatures.

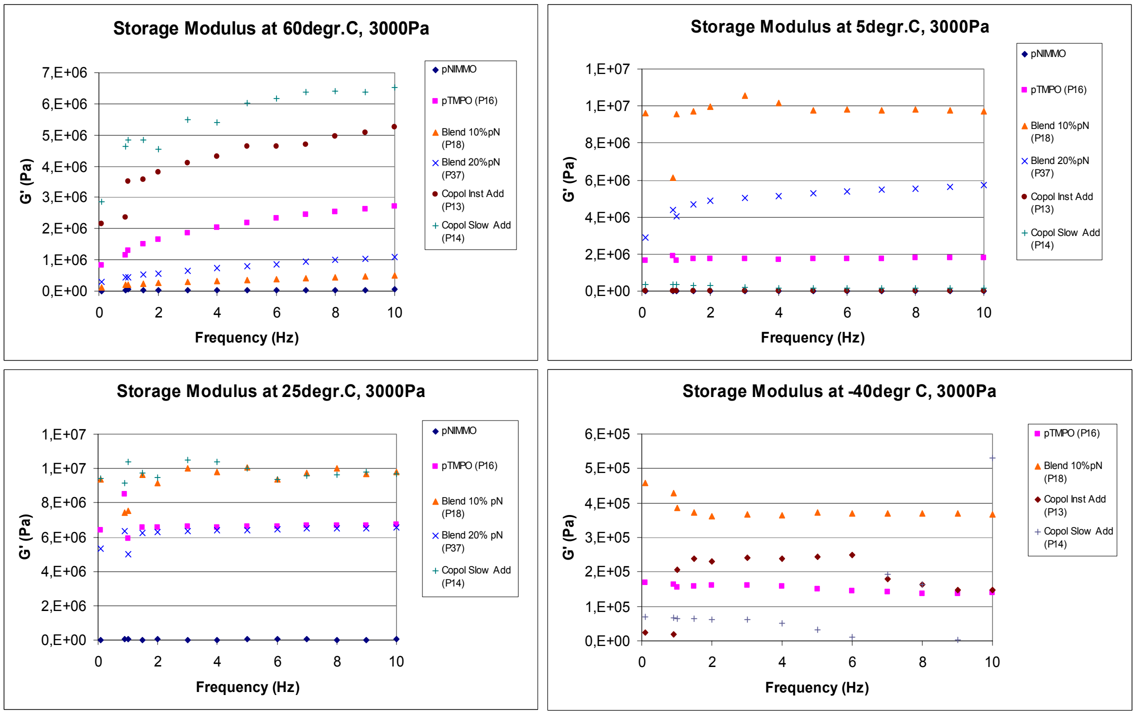


Figure 10. *Results from rheometer analysis showing storage modulus at 60, 25, 5 and -40ºC for the homopolymers, blends and copolymers. PolyNIMMO is not shown in the -40ºC diagram, due to its much higher modulus (G´~7MPa).*

3.2.2. GAP-polyTMPO copolymer

^{1}H-NMR showed no presence of polyTMPO in the reaction product analysed. Obviously GAP-polyTMPO did not copolymerise during the reaction time available. A possible reason could be that the initiator chosen for the reaction had too low reactivity in the GAP-polyTMPO system in combination with the solvent used.

4. Conclusions

4.1. PolyNIMMO-diol copolymers

Reacting polyNIMMO with both PEB and pentanediol was successful. However, the polyNIMMO-PEB mixture showed more promising properties since it starts to melt between 50°C–80°C, which indicates the possibility to melt process the material when adding the oxidiser. The T_g for the copolymers is too high to match the service temperature requirements of -40°C to +60°C. It would therefore be necessary to modify the structure and the addition of a plasticiser could also be necessary. There is also the problem of degassing and filling moulds before the material solidifies. One way to avoid this problem would be to perform the mixing under vacuum and to use preheated moulds when filling them. Since these copolymers are too difficult to melt process at temperatures below 90°C, they are for the moment not suitable for ADN-based propellants.

4.2. PolyNIMMO- hyperbranched polyoxetane

PolyNIMMO-polyTMPO copolymers was formed in the experiments described and were phase separated, i.e. showed TPE properties of a block-copolymer, which has one distinct T_g for the soft segment and one for the stiff segment. It was not possible to determine if a tri-block structure (ABA-structure) had been formed in the copolymer products. The products were most likely a mix of AB- and ABA-block-*co*-polymers.

The method used for molecular weight analysis proved to be insufficient when analysing the copolymers. Polar agglomerates were formed due to a solvation effect, and there is also a built-in underestimation of the molecular weight determination of hyperbranched molecules. These two facts led to difficulties of molecular weight determinations, but still there are no better alternatives.

The polyNIMMO-polyTMPO copolymers formed in the experiments had a quite low energetic content compared to the homopolymer of polyNIMMO to be useful in ADN-matrix applications and the oxygen balance was even more unfavourable than for pure polyNIMMO.

The mechanical properties for the copolymers showed to be acceptable in the temperature interval designated and were significantly better than for the blends and pure polyNIMMO. Especially at the upper temperature limit, the polyNIMMO-polyTMPO blends tended to show fluid-like behaviour, while the copolymers retained their relatively constant elastic properties.

The attempts to increase the energetic content in the copolymers failed in the sense that no more than approximately 20mol% of polyNIMMO could be introduced into the ETPE:s. The cause of these poor results is probably a combination of low reactivity of the polyNIMMO hydroxyl end groups and a low probability of the end groups to get into the right positions to react with the ring-strained TMPO-monomers. Low reactivity of the polyNIMMO end groups is concluded from the fact that high monomer conversions were achieved in the solution polymerisation experiments, without an increase of polyNIMMO-content, which would have been the case if the energetic polymer has had the same reactivity as the TMPO hydroxyl groups.

The exothermal phase transitions observed in the DSC-thermograms and also during rheology analysis might pose a serious limitation to ADN-matrix applications, due to possible crack formation. If the cause is crystallising linear segments in the ETPE, the phase transitions could be avoided by increasing the molecular weight, thereby forming a higher degree of hyperbranching of the polyTMPO-part of the copolymer.

The GAP-polyTMPO system needs to be further investigated for copolymerisation to take place at an acceptable rate. The possibility of evaluating different initiators should be utilized, maybe in combination of higher concentrations of the reagents used.

5. Suggestions of Further Work

5.1. PolyNIMMO-diol copolymers

A new high-shear small scale mixer, working under vacuum, is now available at FOI, and further experiments will be performed on this equipment. With the new mixer it will be possible to perform the experiments under better conditions and thus receive better materials for further analysis. In order to increase the flexibility of the material, it would be interesting to react polyNIMMO and PEB with a different NCO/OH ratio and/or use another ratio between the diol and polyNIMMO. Another interesting approach would be to perform the experiments with GAP instead of polyNIMMO as the soft block of the TPE. This would further increase the energy content of the composition.

5.2. PolyNIMMO- hyperbranched polyoxetane

For the polyNIMMO-polyTMPO-copolymer to be useful as a matrix binder for ADN, the energy content has to be increased significantly in the ETPE in order to avoid dilution of the energetic content of the total formulation. In order to increase the energetic content, the reactivity of the polyNIMMO hydroxyl end groups has to be increased. One method could be to perform further bulk polymerisations using even slower addition of TMPO monomer than made in present experiments. A suggestion could be using an addition time of approximately 10 hours or more. Then, the activated monomer mechanism might dominate the propagation step in the copolymerisation and the result would be an increase in polyNIMMO-content and a higher degree of branching (in theory). Another approach to achieve higher polyNIMMO content in the copolymers could be to use small amounts of functionalised epoxides to react with the hydroxyl groups, preferably in solution polymerisation experiments.

Solution polymerisation experiments with GAP-polyTMPO-copolymers could generate a copolymer with a higher energetic content than for polyNIMMO-*co*-polyTMPO. The use of different initiators, such as BF_3OEt_2, should be evaluated first, to minimise reaction time without compromising safety issues.

An alternative and perhaps a more efficient method of analysing ETPE molecular weights could be to use high performance liquid chromatography (HPLC) in combination with a mass spectrometer (MS). The method could be used for low molecular weight ETPE:s, such as polyNIMMO-polyTMPO produced in present experiments, and it is insensitive to several problems connected with SEC analysis, such as polar agglomerates forming during analysis.

6. References

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7. Appendix

- Appendix 1; Table 4, 5 and 6.
- Appendix 2; Table 7.
- Appendix 3; Table 8.

Appendix 1.

Table 4. *Polymerisations of polyTMPO-polyNIMMO performed in bulk.*

Bulk Polymerisation

Initiator: $BTSSbF_6$

Instant Add (#)	pN:pT[1] (w.r.)	pNIMMO (g)	TMPO (g)	pN/pT[2] (m.r.)	T (°C)	Yield[3] (wt%)	Time (h)	pN Cont[4] (mol%)	M_n[5] (g/mol)
P1	1:1	5,0	5,0	0,79	100		4,5		1741
P9	1:1	10,0	10,0	0,80	105	13	4,5		1844
P10	1:1	5,0	5,0	0,79	110	22	4,5		1821
P11	1:1	5,0	5,0	0,78	110	21	2		1711
P12	1:1	5,0	5,0	0,79	105	17	3,5		1615
P13	1:1	5,0	5,0	0,79	105	12	3	12	1846
P15	1:1	5,1	5,0	0,79	100	9	2,5	10	1730
P26	1:2	1,7	3,4	0,39	100		22	3	1505
Slow Add									
P3	1:1	5,0	5,0	0,79	100	12	4,5		2249
P4	1:1	10,0	10,0	0,79	100	19	4,5	12	1715
P5	1:1	5,0	5,0	0,79	120	11	4,5		1742
P6	2:1	6,7	3,3	1,58	100	8	4,5		1568
P8	1:2	3,3	6,7	0,39	100	27	3,5		2071
P14	1:1	5,0	5,0	0,78	105	13	3	9	1827
Initiator: BF_3OEt_2									
Instant Add									
P22	1:1	2,5	2,5	0,77	100	18	2,5	17	1048
P23	1:1	2,5	2,5	0,79	100	25	5,5	9	1560
P24	1:1	2,5	2,5	0,79	100		22	10	1198
P25	1:1	2,6	2,6	0,79	100	47	4,5	9	1759
P27	1:2	1,7	3,4	0,39	100		5	8	1197

[1] *PolyNIMMO/polyTMPO weight ratio at $t=t_0$*

[2] *PolyNIMMO/polyTMPO molar ratio at $t=t_0$*

[3] *After 1 wash with Ethyl Acetate (EtOAc) or precipitation in same*

[4] *PolyNIMMO content in products. Analysed by ^{1}H-NMR*

[5] *Molecular Weight. Analysed by SEC (DMF)*

Table 5. *Blends of polyTMPO and polyNIMMO performed by mechanical melt mixing.*

Melt Blending

Experiment (#)	pN:pT[1] (w.r.)	pNIMMO (g)	pTMPO (g)	pN/pT[2] (m.r.)	T (°C)	Yield[3] (wt%)	Time (h)	pN Cont[4] (mol%)	Mn[5] (g/mol)
P17	01:08	0,5	4	0,1	140	88	5	13	1406
P18	01:08	1	8	0,1	130	73	4	12	1461
P37	01:04	1	4	0,2	140	75	4,5	21	1514

[1] *PolyNIMMO/polyTMPO weight ratio at $t=t_0$*

[2] *PolyNIMMO/polyTMPO molar ratio at $t=t_0$*

[3] *After 1 wash with EtOAc or precipitation in same*

[4] *PolyNIMMO-content in products. Analyzed by ^{1}H-NMR*

[5] *Molecular Weight. Analyzed by SEC(DMF)*

Table 6. *Copolymerisations performed in solution.*

Solution Polymerisation

Initiator: $BTSSbF_6$

Instant Add (#)	pN/pT[1] (w.r.)	pNIMMO (g)	TMPO (g)	pN/pT[2] (m.r.)	T (°C)	Yield[3] (wt%)	Time (h)	Solvent	pN Cont[4] (mol%)	M_n[5] (g/mol)
P19	1:1	0,51	0,50	0,81	40		4	THF		
P20	1:1	0,50	0,49	0,79	60		20,5	THF		
P21	1:1	0,53	0,51	0,82	60	9	24	THF	23	954
Initiator: BF_3OEt_2										
P28	1:1	0,50	0,51	0,78	55	7	25	$CHCl_3$	10	1017
P29	1:1	0,50	0,51	0,77	40	8	25	$CHCl_3$	12	
P30	1:1	0,50	0,51	0,78	30	12	20	$CHCl_3$	14	871
P31	1:1	0,53	0,53	0,79	0	15	6	$CHCl_3$	20	741
P32	1:1	0,52	0,51	0,80	60	17	23	Toluene	4	1115
P33	1:1	0,51	0,52	0,78	100	8	23	Toluene	13	1282
P34	1:1	0,52	0,53	0,77	60	26	20,5	Toluene	4	1156
P35	1:1	0,51	0,51	0,78	25	16	22	Toluene	7	1121
P36	1:1	0,49	0,51	0,77	0	12	21	Toluene	9	943

[1] *PolyNIMMO/polyTMPO weight ratio at $t=t_0$*

[2] *PolyNIMMO/polyTMPO molar ratio at $t=t_0$*

[3] *After 1 wash with EtOAc or precipitation in same*

[4] *PolyNIMMO-content in products. Analyzed by ^{1}H-NMR*

[5] *Analyzed by SEC (DMF)*

Appendix 2.

Table 7. Solubility tests. ~100mg sample dissolved in 20mL vials.

Solvent:	**ε[1]:**	**pNIMMO:**	**TMPO[2]:**	**pTMPO[3]:**
n-Hexane	1.9	Insoluble	Insoluble	Insoluble
Toluene	2.4	Soluble	Soluble	Partly
Diethylether	4.3	Partly	Soluble	Insoluble
$CHCl_3$	4.8	Soluble	Soluble	Partly
EtOAc	6.0	**Soluble**	Insoluble	Insoluble
1,2-dimetoxiethane	7.2	Soluble	Soluble	Insoluble
THF	7.6	Soluble	Soluble	Soluble
CH_2CH_2	8.9	Soluble	Soluble	Insoluble
1-butanol	17.5	Insoluble	Insoluble	**Soluble**
2-propanol	19.9	Insoluble	Insoluble	**Soluble**
Acetone	20.7	Soluble	Insoluble	Insoluble
Ethanol(95%)	24.6	Insoluble	Soluble	Soluble
Methanol	32.7	Insoluble	Insoluble	Soluble
DMF	36.7	Soluble	Soluble	Soluble
Acetonitrile	37.5	Soluble	Insoluble	Insoluble
DMSO	46.7	Soluble	Soluble	Soluble
H_2O	78.4	Partly	Insoluble	Insoluble

[1] Dielectricity constant values are given for the different solvents to illustrate differences in solvent polar properties. These values, however, cannot be directly related to the solubility of the different materials. [2] ~100mg sample in 2mL vials. [3] Sample from experiment P7.

Appendix 3.

Table 8. *A comparison of polyNIMMO-content in copolymer products and blends, after wash with EtOAc, using two different methods: ^{1}H-**N**MR and FT-IR (ATR).*

Bulk Polymerisation	**Analysis Method**		
Initiator: BTSSbF$_6$ **Instant Addition (#)**	**NMR pN-content (mol%)**	**IR[1] pN-content (mol%)**	**NMR/IR Relative Ratio (%)**
P13	12,4	19,1	65
P15	10,0	12,2	82
P26	2,5	11,1	22
Slow Addition			
P4	12,0	25,0	48
P14	8,8	16,4	54
Initiator: BF$_3$OEt$_2$ **Instant Addition**			
P22	16,7	48,7	34
P24	9,5	31,8	30
P25	9,3	19,3	48
P27	7,7	35,6	22
Solution Polymerisation			
Initiator: BTSSbF$_6$ **Instant Addition**			
P21	23,3	43,3	54
Initiator: BF$_3$OEt$_2$ **Instant Addition**			
P28	10,1	4,5	224
P29	11,9	17,2	69
P30	14,3	20,8	69
P31	19,6	26,5	74
P32	3,6	5,1	71
P34	3,8	7,7	49
P35	7,2	14,5	50
P36	9,2	21,9	42

[1] *Mean value of three analyses per sample (IR).*