

## Mechanical Properties of Smokeless Composite Rocket Propellants Based on Prilled Ammonium Dinitramide

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### Abstract

Ammonium dinitramide (ADN) is a high performance solid oxidizer of interest for use in high impulse and smokeless composite rocket propellant formulations. While rocket propellants based on ADN may be both efficient, clean burning and environmentally benign, ADN suffers from several notable disadvantages such as pronounced hygroscopicity, significant impact and friction sensitivity, moderate thermal instability and numerous compatibility issues. Prilled ADN is now a commercially available and convenient product that addresses some of these disadvantages by lowering the specific surface area and thereby improving handling, processing and stability. In this work, we report the preparation, friction and impact sensitivity and mechanical properties of several smokeless propellant formulations based on prilled ADN and isocyanate cured and plasticized glycidyl azide polymer (GAP) or polycaprolactone. We found such propellants to possess very poor mechanical properties in unmodified form and to display somewhat unreliable curing. However, by incorporation of cyclotetramethylene tetranitramine (HMX) and a neutral polymeric bonding agent (NPBA), the mechanical properties of such smokeless formulations were significantly improved. Impact and friction sensitivities of these propellants compare satisfactorily with conventional propellants based on ammonium perchlorate (AP) and inert binder systems.

**Keywords:** Propellant, ADN, HMX, GAP, NPBA

## 1 Introduction

Ammonium perchlorate (AP), most often used in combination with finely divided aluminium and isocyanate cured hydroxyl-terminated polybutadiene (HTPB), firmly remains the basis for most solid composite rocket propellants due to its reliable, adjustable and good ballistic performance, as well as its convenient availability and reasonable cost [1,2]. However, due to the development of copious quantities of visible hydrogen chloride in the exhaust plume during combustion, the AP content must be kept at an absolute minimum in low signature propellant

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formulations. Few alternative and relevant oxidizers are available for replacement of AP in smokeless composite propellants.

Ammonium nitrate (AN) is a low sensitive and alternative oxidizer to AP that is both environmentally benign and inexpensive. Unfortunately, it suffers from increased hygroscopicity and low specific impulse relative to AP, but even worse, it exhibits a very moderate burn rate. It also undergoes several solid-state phase transitions at low to moderate temperatures, giving unwanted volume alterations that are difficult to control during curing and storage [2]. It therefore tends to be used as an additive to lower the sensitivity rather than being the main oxidizing component in composite propellant formulations. Nitramines, like RDX and HMX, are also alternatives to AP as main components in smokeless propellants. They have high specific impulse, but are moderately sensitive and have a slightly negative oxygen balance and are therefore unable to contribute positively to the oxygen balance of the propellant. In addition, unlike AP and AN, nitramines are chemically relatively inert and are therefore nonreactive towards traditional bonding agents, giving poor mechanical characteristics in the cured propellants. Neutral polymeric bonding agents (NPBA) are bonding agents that have been developed to overcome these adhesion issues in formulations using nitramines in polar binder systems [3-5]. We have recently shown how such bonding agents can be successfully utilized in smokeless composite propellants based on the nitramine HMX, the energetic binder GAP and the energetic plasticizer *N*-butyl-2-nitrateethylnitramine (BuNENA) [6].

Ammonium dinitramide (ADN) is a relatively new high performance solid oxidizer that combines a high burn rate with the advantageous oxygen balance and clean burning properties of AN [2,7]. It was first prepared in the Soviet Union in the early 1970s and has been in development in the western world since the 1990s [2,7]. Its synthesis has been extensively investigated and the material is today commercially available from Eurenco Bofors in Sweden [7]. Unfortunately, the widespread utilization of ADN is hampered by its considerable hygroscopicity, being even substantially more pronounced than for AN, its poor thermal stability and relatively high sensitivity, but probably even more due to its numerous compatibility issues, and then especially with isocyanates [7]. In order to overcome some of these limitations, prilled ADN has been developed by the Swedish Defence Research Agency (FOI) in Sweden, and is now a commercially available product from Eurenco Bofors under license from FOI.

While introduction of prilled ADN to a certain extent remedies the substantial water affinity of ADN due to the decreased surface area of the prills relative to the native needle shaped crystals of ADN, it is not well known how such large prills, several hundred micrometers, will affect the mechanical properties of the cured propellants. Although decreased surface area is obviously advantageous with regards to water uptake, the prills also give rise to large discontinuities in the elastomer structure because of their size. This may adversely affect important mechanical parameters of the cured propellant such as tensile strength, elongation and elastic modulus. While thermal decomposition, combustion characteristics, impulse calculations and ballistic performance for ADN compositions have been widely studied [8-13], mechanical properties of rocket propellants based on ADN have almost never been discussed in the open literature [9,13].

Herein, we report our work on the use of prilled ADN in smokeless composite propellants based on plasticized and isocyanate cured glycidyl azide polymer (GAP) or hydroxyl-terminated caprolactone ether (HTCE) binder. We discuss how the prilled ADN will affect processing and curing of the propellant mixtures, as well as the mechanical properties of the cured propellants.

As it is well known that ADN has serious compatibility issues with many isocyanates, we also studied the effects of incorporating previously reported stabilizers on the curing properties. We will then proceed to detail how we can improve the mechanical properties by incorporating HMX and a suitable bonding agent into the propellant formulation.

## 2 Experimental

### 2.1 Chemicals

Prilled ADN was purchased from Eurenco Bofors - FOI. Representative data for prilled ADN: Mp. 92.4 °C, density = 1.796 g/cm<sup>3</sup>, size distribution with 10% below 52 μm, 50% below 195 μm and 90% below 362 μm. GAP diol prepolymer and GAP azide plasticizer were acquired from Eurenco (France), the curing agents Desmodur N100 from Bayer MaterialScience (Germany) and isophorone diisocyanate (Vestanat IPDI) from Evonik Industries and the curing catalyst triphenyl bismuth (TPB) from AproS Corporation (South Korea). The plasticizer BuNENA and nitramine HMX were obtained from Chemring Nobel AS (Norway), trimethylolethane trinitrate (TMETN) plasticizer from SNPE (France), polycaprolactone (HTCE) from Solvay Interlox (Great Britain) and polyethylene glycol (PEG) – polypropylene glycol (PPG) polyether polyol (Voranol) from Dow Chemical. Dibutyltin dilaurate (DBTDL), stabilizers and other materials were acquired from standard laboratory suppliers. The neutral polymeric bonding agent (NPBA) was synthesized as described by us previously [6]. It is a copolymer of acrylonitrile, methyl acrylate and 2-hydroxyethyl acrylate in the monomer ratio 1.0:0.30:0.20 prepared by free radical solution copolymerization in acetone. GPC analysis (DMF/0.01 M LiBr, PMMA calibration):  $M_n = 4330$ ,  $M_w = 8840$ , PDI = 2.04 [6].

### 2.2 Instruments and Analysis

Small scale propellant mixtures (20-70 g) were prepared in a remotely controlled custom made mini-mixer made of glass and equipped with a fluoropolymer stirring paddle. Larger scale propellant mixtures were prepared in an IKA vertical mixing system HKV-1. Mechanical tensile testing was conducted with an 810 MTS (Material Testing System) according to the procedure of STANAG 4506. Dynamic mechanical analysis (DMA) was carried out using a TA Instruments DMA 2980 and differential scanning calorimetry (DSC) was carried out with a TA Instruments DSC Q1000. Rheology measurements were performed using a Paar Physica UDS 200 with MP30 spindle (25 mm, 0°). Infrared (IR) spectroscopy during propellant curing was performed with a Nicolet Avatar 320 FTIR ATR. The Shore A hardness was measured with a Bareiss BS61 durometer. Vacuum thermal stability (VTS) testing was done according to STANAG 4556.

### 2.3 Preparation of Composite Rocket Propellants

HMX was dried at 60 °C for a minimum of 72 h prior to use while prilled ADN was used as received. Standard mixing and vacuum casting techniques have been used in producing these propellants. When using NPBA, it was dissolved in plasticizer over night at 60 °C before mixing. The filler particles were dispersed in a submix consisting of binder, plasticizer, NPBA and other

minor components and stirred at 55 °C. The curing agent and curing catalyst were subsequently added and the mixture was casted under vacuum. The propellant was then allowed to cure (curing conditions will be detailed in later sections). The curing reaction was followed by IR spectroscopy and rheology.

### 3 Results and Discussion

#### 3.1 Compatibility Testing of Prilled ADN with Binders, Plasticizers and Isocyanates

ADN is known to possess serious compatibility issues with several conventional solid rocket propellant components such as isocyanates and also certain binders and nitrate ester plasticizers [7]. We tested the compatibility of prilled ADN by vacuum thermal stability (VTS), either by itself at varying temperatures or in mixtures with GAP or some conventional isocyanates or plasticizers at 80 °C. The results are presented in Table 1. As expected, prilled ADN was clearly incompatible with isocyanates like Desmodur N100 and IPDI at 80 °C, rapidly giving expanded soft foams.

<tabr1>

It is known that ADN is at least partially incompatible with many nitric acid esters such as poly(glycidyl nitrate) (PGN) and BuNENA [7]. We found prilled ADN to be incompatible with both BuNENA and TMETN at 80 °C according to our VTS testing. Supporting existing data [7], we also found prilled ADN to be compatible with typical GAP derivatives like GAP diol and GAP azide. Although ADN is reported to be compatible with binders like HTPB or poly(3-nitratomethyl-3-methyloxetane) (PolyNiMMO), it has a problematic compatibility with many polyether binders due to their acidic nature [7], and the compatibility with HTPB can be endangered in the presence of air. ADN is known to actually have a substantial solubility in some polyethers [13], further complicating the use of polyether binders for ADN propellants. As part of our own testing, we found a standard Voranol PEG-PPG polyether to be compatible with ADN at 80 °C (Table 1).

While we found prilled ADN to have compatibility issues with isocyanates and BuNENA and TMETN plasticizer, we considered these problems to be much lower at mixing and curing temperatures (20-60 °C), allowing safe propellant preparation. Due to the good compatibility of prilled ADN and GAP derivatives, as well as the known favourable ballistic performance of such propellants [8], we decided to base most of our ADN-containing smokeless propellants on GAP binder. We then used additions of polyethers or HTCE in an attempt to improve the mechanical properties of our compositions.

#### 3.2 Small Scale Propellant Formulations with Prilled ADN and GAP

Given the favourable compatibility of ADN and GAP derivatives, our first propellant formulation using prilled ADN was based on GAP diol binder and GAP azide plasticizer according to the composition given in Table 2. A small amount of PEG-PPG polyether was used to improve the elastomer strength. The propellant was prepared on small scale in a remotely

controlled custom made mini-mixer and cured at room temperature using DBTDL (~100 ppm) as curing catalyst.

<tabr2>

Mechanical testing of the propellant prepared according to Table 2 using end-bonded propellant samples indicated a maximum tensile strength of approximately 0.20 MPa, an elastic modulus of 2 MPa and elongation at break around 21%, in essence very poor mechanical properties, but rather typical for ADN propellants [9]. In order to improve mechanical properties, modifications with bonding agents and/or additional filler materials are clearly needed. Curing of these ADN-containing propellants is unreliable and the additional components we had in mind required the use of more conventional nitrate ester plasticizers. For that reason, we prepared a number of small scale mixtures based on prilled ADN, GAP diol and one of the energetic plasticizers GAP azide, TMETN or BuNENA. The curing behaviour of these mixtures at different temperatures and with different curing catalysts was studied.

Isocyanate curing of ADN-containing propellants is known to be problematic as ADN possesses only a partial compatibility with many of the conventional isocyanates used in rocket propellants [9,13]. Menke and coworkers have studied the curing behaviour of ADN-GAP propellants in detail [9]. They thoroughly investigated decomposition products and proposed decomposition mechanisms and developed a mixture of three stabilizers to aid successful curing at 60°C [9]. Extending knowledge from literature [10-12], a zeolite was added for removal of water and ammonia and *N*-methyl-*p*-nitroaniline (MNA) was added for neutralization of acids at the surface of ADN particles. In addition, a traditional nitrate ester stabilizer like Akardite was added as the propellants were based on nitrate ester plasticizer [9]. Accordingly, we used a mixture of MNA, zeolite and an Akardite type analogue (*N,N'*-diphenylurea) as stabilizers in our propellant formulations. As will be pointed out later, in the end we did not find these stabilizers especially helpful for improved curing and subsequently did not include them in our last two larger scale formulations.

Several propellant formulations with a 60% solid loading of prilled ADN with GAP diol binder and either GAP azide, TMETN or BuNENA plasticizer were prepared in our mini-mixer on ~50 g scale, using 1% each of MNA, zeolite and diphenylurea as stabilizers. Their curing behaviour was studied at room temperature and 60 °C, using triisocyanate N100 as curing agent and either TPB or DBTDL as curing catalysts.

All samples containing BuNENA plasticizer gave a non-satisfactory soft cure, meaning a soft and expanded porous texture in the cured propellant samples. This is not surprising given that the compatibility of ADN and BuNENA is poor. More interestingly though was the somewhat variable and unreliable curing behaviour exhibited by the other samples. Use of TPB as curing catalyst was mostly invariably associated with unsuccessful soft cure, most probably due to its moderate catalytic activity, giving ample time for side reactions to compete during cure. DBTDL was therefore the preferred curing catalyst, giving reliable results when utilized in the TMETN plasticized formulations and cured at room temperature. However, analogous samples cured at 60 °C furnished unpredictable curing results, very often resulting in unsuccessful soft cure, probably indicative of autocatalytic processes since very small variations in initial conditions resulted in such dissimilar end results. Even completely identical samples could cure successfully at room temperature, but exhibit unpredictable and sometimes unsuccessful soft cure at 60 °C when

placed in different containers. Our preferred protocol for all large scale preparations was subsequently based on a rapid propellant cure at room temperature for 24 h using rather generous quantities of DBTDL curing catalyst (50 – 150 ppm), giving a potlife of approximately 5 h for the propellant mixtures.

<tabr3>

One final small scale propellant was prepared according to the composition given in Table 3, based on GAP diol and TMETN plasticizer, and cured at room temperature with DBTDL curing catalyst. In addition, we included a neutral polymeric bonding agent (NPBA) analogous to those we have reported recently for use in HMX-GAP-BuNENA propellants [6]. Mechanical testing of the propellant using end-bonded propellant samples indicated a maximum tensile strength of approximately 0.27 MPa, an elastic modulus of 5.3 MPa and elongation at break around 15%, somewhat improved relative to that of Table 2, but still rather poor mechanical properties. As a result, we decided to proceed by including a portion of HMX in the propellants of our larger scale trials as we knew that HMX in GAP binder using NPBA would most probably provide improved mechanical properties [6].

### **3.3 Mechanical Properties of Smokeless Propellants Based on Prilled ADN and HMX**

As disclosed in our small scale trials, smokeless propellant formulations based on prilled ADN-GAP in general had markedly poor tensile strengths. However, a useful plasticizer (TMETN) and reliable curing conditions (DBTDL at room temperature) for these ADN-GAP-TMETN based compositions had been identified. To probe mechanical properties in more detail and obtain more reliable data than those possible from the small end-bonded samples, we prepared three propellant formulations on larger scale, based on prilled ADN, isocyanate cured binder and TMETN plasticizer, this time at 500-1000 g scale in a conventional mixer. Three such propellants with 60% solid loading, labelled propellant A, B or C, are detailed in Table 4. In order to improve mechanical properties, a quarter of the prilled ADN was substituted with HMX of two particle fractions relative to our previous small scale trials. Propellant A is based solely on GAP binder while propellant C is based on hydroxyl-terminated caprolactone ether (HTCE). The use of HTCE in ADN propellants is well-known [11-13], but such polyester polyethers usually give rise to rather stiff propellant composites, and we wanted to compare it to our GAP based formulation. The compatibility of HTCE and prilled ADN was of course confirmed by DSC analysis prior to its introduction. In propellant B, the use of GAP is accompanied with a small quantity of HTCE to improve sample stiffness.

In propellants A, B and C, NPBA was included to improve filler-matrix adhesion in line with our previous work on HMX-GAP propellants [6]. Propellant A contains the three stabilizers detailed above, but as we later became convinced about the fact that the stabilizer system was of limited use, we did not include the stabilizers in propellant formulations B and C. We had used an isocyanate hydroxyl curing ratio of 1.0 in our small scale trials, but as some isocyanate may be consumed in unwanted side reactions during cure according to suggested decomposition pathways [9], we used curing ratios of 1.15-1.30 in propellants A, B and C.

<tabr4>

<figr1>

<figr2>

<figr3>

The ADN propellants A to C, as our previous smaller scale formulations, generally processed very well at these low solid loadings. The rounded prilled ADN definitely afforded an advantageous processability to these formulations and will allow for much higher solids loading than 60% in future work. After curing, propellant samples were prepared for tensile testing and the stress-strain curves for propellants A to C are given in Figures 1-3. Their mechanical and thermal characteristics are summarized together with their chemical compositions in Table 4.

As can be seen from Figures 1-3 and Table 4, the propellants A, B and C all have significantly improved mechanical properties, roughly doubling tensile strengths relative to our earlier formulations without HMX and NPBA. The stress-strain curves also take on a slightly peculiar and interesting overall shape where there seems to be a slight necking type effect at low elongations, followed by a very slight decrease in stress before a near linear relationship of stress-strain is again established and kept up to the point of maximum tensile strength and eventual sample fracture. This is most probably associated with the two types of filler-binder adhesion existing in these formulations where adhesion of the prilled ADN and binder matrix is poorer than adhesion of the smaller HMX particles and binder matrix. The NPBA is also designed with a specific non-covalent interaction of the Lewis acidic HMX surface and Lewis basic NPBA in mind [6], while this is not being the case relative to ADN. For a more in-depth discussion of nitramine filler and polar binder system adhesion issues, our previous report and references contained therein should be consulted [6].

Glass transition temperatures as measured by DMA analysis are decreasing when going from propellant A to B to C, which is in line with our expectations as propellant A is based solely on GAP binder while propellant B contains some added HTCE and propellant C is based solely on HTCE. This reflects the known characteristics of these binder systems. As can be seen from Table 4, even small quantities of HTCE result in a considerable increase of elastic modulus relative to GAP binder. Propellant C, based solely on HTCE binder, also has somewhat increased elongation at break relative to the GAP or GAP-HTCE binder systems in propellants A and B. Other researchers have reported the use of nitrocellulose as crosslinkers for improving the mechanical characteristics of ADN propellants [13], something that has not been pursued in this work.

### **3.4 Sensitivity of Composite Propellants based on Prilled ADN**

ADN was first synthesized in 1971 at the Zelinsky Institute of Organic Chemistry in Moscow, and it has been claimed that it might be in actual operational use in Russian Topol intercontinental ballistic missiles based on solid propellant [8]. For use in such large rocket motors, a reasonable level of sensitivity is obviously necessary, but ADN and its composites are generally known for their relatively high level of both impact and friction sensitivity, being comparable to those for RDX and HMX. Prilled ADN however has a more favourable sensitivity profile than native ADN [7].

We tested both the impact and friction sensitivity of propellants A, B and C, all containing both prilled ADN and HMX, as well as the smaller scale formulation without HMX prepared according to the composition in Table 2. These data are presented in Table 4 for propellants A to C and in a footnote to Table 2 for the HMX free composite. We found the friction sensitivity of the ADN composite in Table 2 to be higher than that for the ADN-HMX propellants A to C. However, the impact sensitivities of propellants A to C were significantly higher than that for the ADN composite of Table 2. The incorporation of HMX therefore appears to increase the impact sensitivity relative to the use of prilled ADN alone, while the friction sensitivity is reduced. The substantial friction sensitivity of an ADN-GAP composite has been noted by other researchers as well [7]. Our observation that incorporation of HMX reduces friction sensitivity is therefore interesting.

In order to put the impact and friction sensitivity of our ADN propellants in proper context, a comparison to conventional AP-HTPB based propellants may be helpful. At NAMMO Raufoss, several AP-HTPB propellants with approximately 85% AP and roughly 15% HTPB - dioctyl sebacate (DOS) binder systems (isocyanate cured) are produced commercially. In general, they have impact sensitivities in the range of 1.5 – 4.0 Nm (with predominance in the 3.0 – 4.0 Nm range) and friction sensitivities in the range of 30 – 120 N (with predominance in the 40 – 50 N range), tested in the same apparatus as the ADN propellants in Table 2 and Table 4. Comparing these with the data for ADN-HMX propellants A to C in Table 4, it can readily be seen that they have fairly equal impact sensitivities to the commercial AP-HTPB propellants, and in fact rather reduced friction sensitivities. Our HMX-free ADN propellant (Table 2) has lower friction sensitivity than the ADN-HMX propellants as discussed previously, but nearly equal to most AP-HTPB propellants. As such, composite smokeless propellants based on ADN may have the potential to compete advantageously with standard AP propellant formulations in current use, and indeed also with crosslinked and elastomer modified double base propellant formulations. That said, the thermal stability of our ADN propellants is significantly poorer than for AP propellants with inert binders, which typically can have an onset of exotherm nearly 100 degrees higher than those for propellants A to C (see DSC results in Table 4). Hopefully, expanded testing, including sympathetic detonation and long-term stability, can be conducted in the future to shed more light on the safety of ADN propellants.

## 4 Conclusions

Unmodified composite propellants based on prilled ADN, GAP binder and energetic nitrate ester plasticizers had poor mechanical properties with tensile strengths typically only barely exceeding 0.20 MPa. The tensile strength could be significantly improved by incorporation of HMX and a neutral polymeric bonding agent suited for HMX in GAP binder, affording an approximate doubling of tensile strength. ADN in general had somewhat unpredictable compatibility issues and curing properties with isocyanates, especially at slightly elevated temperatures, and the addition of stabilizers provided non-detectable improvements. Mechanical characteristics of the ADN propellants were clearly improved by addition of HMX and NPBA. The impact sensitivity of such ADN-HMX propellants increased relative to propellants containing only prilled ADN, but the friction sensitivity was reduced. In general, the impact and friction sensitivities are comparable to conventional AP-HTPB propellants.



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### Symbols and Abbreviations

ADN	ammonium dinitramide = $\text{NH}_4\text{N}(\text{NO}_2)_2$
AN	ammonium nitrate
AP	ammonium perchlorate
BuNENA	<i>N</i> -butyl-2-nitrateethylnitramine
Desmodur N100	hexamethylene diisocyanate biuret trimer
DBTDL	dibutyltin dilaurate
DMA	dynamic mechanical analysis

DMF	<i>N,N</i> -dimethylformamide
DOS	dioctyl sebacate
DSC	differential scanning calorimetry
FOI	Swedish Defence Research Agency
GAP	glycidyl azide polymer
GPC	gel permeation chromatography
HMX	octogen, cyclotetramethylene tetranitramine
HTCE	hydroxyl-terminated caprolactone ether
HTPB	hydroxyl-terminated polybutadiene
HTPE	hydroxyl-terminated polyether
IPDI	isophorone diisocyanate
IR	Infrared
$M_n$	number average molecular weight
$M_w$	weight average molecular weight
MNA	<i>N</i> -methyl- <i>p</i> -nitroaniline
NPBA	neutral polymeric bonding agent
PDI	polydispersity index
PEG	poly(ethylene glycol)
PGN	poly(glycidyl nitrate)
PMMA	polymethylmethacrylate
polyNiMMO	poly(3-nitratomethyl-3-methyloxetane)
PPG	poly(propylene glycol)
RDX	hexogen, cyclotrimethylene trinitramine
TMETN	trimethylolthane trinitrate
TPB	triphenyl bismuth
VTS	vacuum thermal stability

## Table Captions

**Table 1.** Vacuum thermal stability (VTS) testing at 80 °C for 40 h of prilled ADN and some conventional solid rocket propellant ingredients.

Substance(s)	Gas volume [cm <sup>3</sup> / 5 g]
ADN <sup>a)</sup>	>5
ADN <sup>b)</sup>	0.50
ADN/GAP Diol	0.38
ADN/PEG-PPG	0.79
ADN/N100	>5
ADN/IPDI	>5
ADN/BuNENA	>5
ADN/GAP Azide	0.69
ADN/TMETN	>5

a) At 100 °C. b) At 70 °C.

**Table 2.** First trial for small scale smokeless rocket propellant composition based on prilled ADN.<sup>a)</sup>

Constituent	Percentage [wt%]
Prilled ADN	60.0
GAP Diol	20.0
PEG-PPG	3.2
GAP Azide	13.5
N100	3.3

<sup>a)</sup> Prepared on 20-70 g scale in remotely controlled custom made mini-mixer. Cured with DBTDL at room temperature with cure ratio NCO/OH = 1.0. An impact sensitivity of 6 Nm and friction sensitivity of 42 N were measured according to UN in BAM apparatus.

**Table 3.** Small scale smokeless rocket propellant composition based on prilled ADN with bonding agent.<sup>a)</sup>

Constituent	Percentage [wt%]
Prilled ADN	60.1
GAP Diol	22.4
TMETN	11.6
N100	3.6
MNA	0.7

Zeolite	0.7
<i>N,N'</i> -Diphenylurea	0.7
NPBA	0.2

<sup>a)</sup> Prepared on 20-70 g scale in remotely controlled custom made mini-mixer. Cured with DBTDL at room temperature with cure ratio NCO/OH = 1.0.

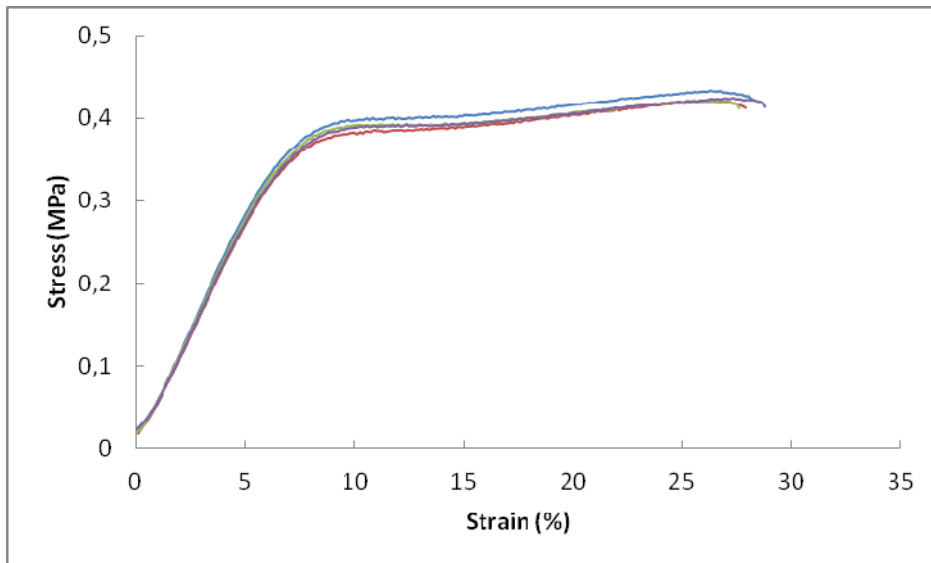
**Table 4.** Smokeless composite rocket propellants based on prilled ADN and HMX.<sup>a)</sup>

Constituent	Propellant A [wt%]	Propellant B [wt%]	Propellant C [wt%]
Prilled ADN	45.0	45.0	45.0
GAP Diol	25.2	23.4	-
HMX (50-60 $\mu\text{m}$ )	9.0	5.0	12.3
HMX (4-5 $\mu\text{m}$ )	6.0	10.0	2.6
TMETN	8.0	8.1	8.0
N100	4.5	4.8	4.4
IPDI	-	-	1.3
HTCE	-	3.5	26.2
MNA	0.7	-	-
Zeolite	0.7	-	-
<i>N,N'</i> -Diphenylurea	0.7	-	-
NPBA	0.2	0.2	0.2
<b>Mechanical properties (21 °C)</b>	<b>Propellant A</b>	<b>Propellant B</b>	<b>Propellant C</b>
Max tensile strength [MPa]	0.42	0.48	0.50
Strength at break [MPa]	0.40	0.44	0.49
Elongation at $\sigma_{\text{max}}$ [%]	26.5	23.0	35.0
Elongation at break [%]	28.3	23.6	35.2
Elastic modulus [MPa]	5.6	9.0	8.4
Shore A hardness	69	92	80
<b>Thermal properties</b>			
$T_g$ DMA 1 Hz [°C]	-38.0	-46.0	-60.0
DSC onset exotherm [°C] <sup>b)</sup>	158.8	158.3	156.4
DSC initial onset exotherm [°C] <sup>b)</sup>	139.0	136.4	131.0
<b>Calculated properties<sup>c)</sup></b>			
Specific impulse [(m/s)/kg]	2334	2312	2048
Characteristic exhaust velocity [m/s]	1494	1480	1264
<b>Impact sensitivity<sup>d)</sup> [Nm]</b>	2.5	3.5	2.5
<b>Friction sensitivity<sup>d)</sup> [N]</b>	72	84	120

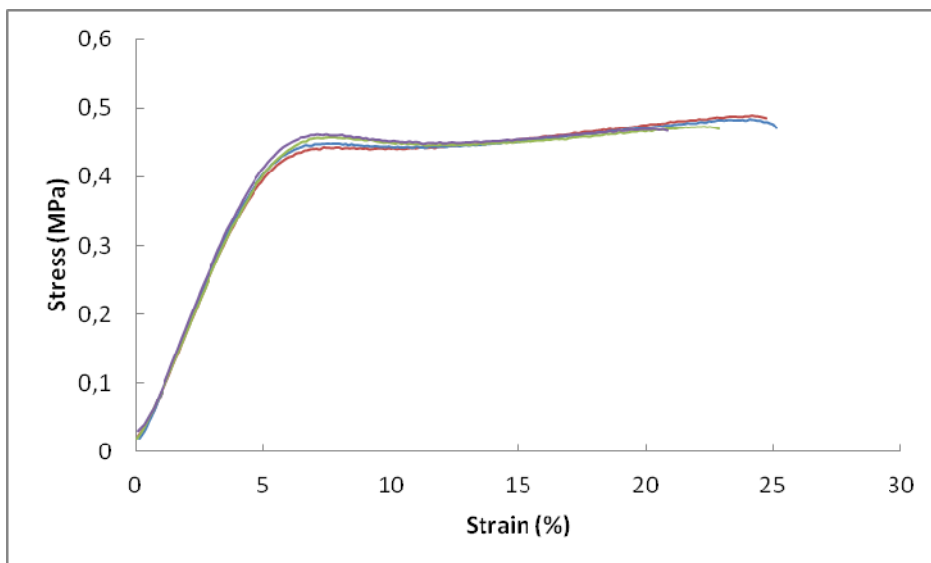
<sup>a)</sup> Propellants A, B and C were all prepared on 500-1000 g scale and cured with DBTDL at room temperature. Cure ratios NCO/OH = 1.30 (propellant A), 1.15 (propellant B) and 1.30 (propellant C). Drawing speed = 50 mm/min for mechanical tensile testing. <sup>b)</sup> Heat rate = 10 °C/min. <sup>c)</sup>

Calculated with computer software<sup>14</sup> at a chamber pressure = 1000 psia and nozzle-expansion ratio = 70:1. Hydroxyl-terminated polyether (HTPE) has been used as a substitute for HTCE in these calculations. <sup>d)</sup> Determined according to UN in BAM apparatus.

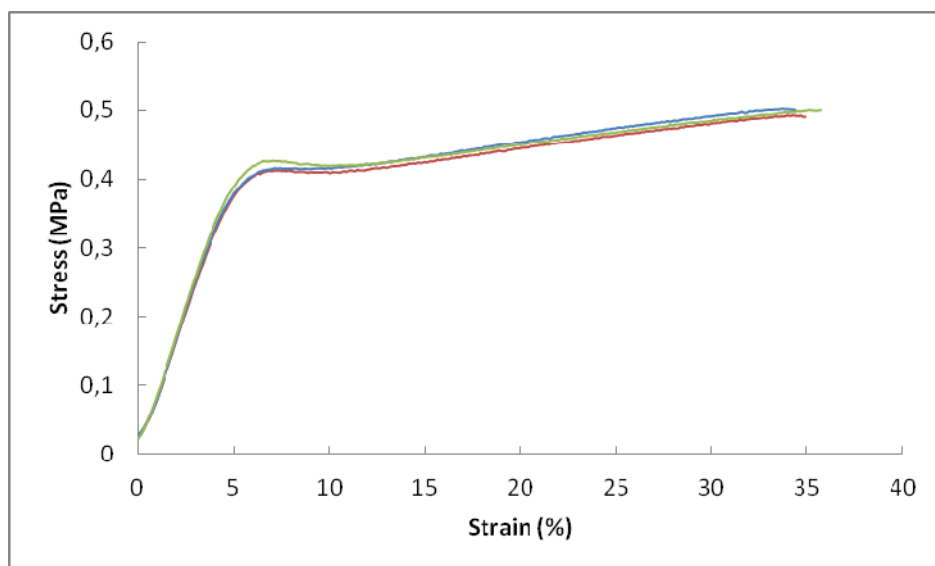
## Figure Captions



**Figure 1.** Tensile testing of ADN-HMX-GAP-TMETN composite (propellant A) with stabilizers and NPBA at 21 °C (4 replicates).



**Figure 2.** Tensile testing of ADN-HMX-GAP-HTCE-TMETN (propellant B) composite propellant with NPBA at 21 °C (4 replicates).



**Figure 3.** Tensile testing of ADN-HMX-HTCE-TMETN composite (propellant C) with NPBA at 21 °C (3 replicates).