

## Neutral Polymeric Bonding Agents (NPBA) and Their Use in Smokeless Composite Rocket Propellants Based on HMX-GAP-BuNENA

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### Abstract

Very few efficient bonding agents for use in solid rocket propellants with nitramine filler materials and energetic binder systems are currently available. In this work, we report the synthesis, detailed characterization and use of neutral polymeric bonding agents (NPBA) in isocyanate cured and smokeless composite rocket propellants based on the nitramine octogen (HMX), the energetic binder glycidyl azide polymer (GAP) and the energetic plasticizer *N*-butyl-2-nitrateethylnitramine (BuNENA). These polymeric bonding agents clearly influenced the viscosity of the uncured propellant mixtures and provided significantly enhanced mechanical properties to the cured propellants, even at low NPBA concentrations (down to 0.001 wt% of propellant). A modified NPBA more or less free of hydroxyl functionalities for interactions with isocyanate curing agent provided the same level of mechanical improvement as regular NPBA containing a substantial number of reactive hydroxyl groups. However, some degree of reactivity towards isocyanate is essential for function.

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

## 1 Introduction

A typical solid rocket propellant is an elastomeric composite material composed of solid particles (oxidizer, fuel and minor additives for adjustment of mechanical or combustion characteristics) suspended in a plasticized polyurethane rubber matrix [1,2]. For most purposes, such a 'state-of-the-art' composite propellant consists of solid ammonium perchlorate (AP) oxidizer, aluminum fuel particles and additives (burning rate modifiers, curing catalysts, stabilizers etc.), all thoroughly mixed with liquid hydroxyl-terminated polybutadiene (HTPB) and a nonpolar plasticizer. The propellant is subsequently cured by addition of a polyfunctional aliphatic isocyanate.

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In order to attain useful mechanical properties such as adequate tensile strength, elastic modulus and elongation in the cured composite propellant, a good adhesion of the solid particles constituting the bulk of the composite material and the continuous binder matrix is critical. To affect good adhesion in AP-HTPB type propellants, a bonding agent is introduced during the preparation, an agent that adsorbs onto the solid particles and attaches them to the rubber matrix network during curing by reaction with the curing agent. For AP propellants, the preferred bonding agent is the alkaline amine compound tetraethylenepentamine acrylonitrile glycidol adduct (Tepanol) or closely related amine compounds [3,4]. Tepanol, in nature of being a highly polar amine, is poorly soluble in the nonpolar polybutadiene matrix, and it adsorbs and reacts at the surface of AP particles in a cation exchange reaction, releasing ammonia and binding firmly to the particle surface [3]. Upon isocyanate curing, reactive (excess) amine and pendant hydroxyl functionalities crosslink and become covalently attached to the continuous rubber matrix. The crosslinked and bonded Tepanol coating then gives rise to what can be referred to according to current paradigm as a covalent shell reinforcement effect, securing the adhesion of particles and rubber matrix and thereby strengthening the overall composite propellant. A second preferred type of bonding agents for AP containing composite propellants is the aziridine family of bonding agents [3,5-7]. For these bonding agents, polymeric shells are presumably formed directly around the AP particles by homopolymerization of aziridines catalyzed by AP [3]. Unfortunately, aziridines, like many of the closely related family of epoxides, are often associated with severe health issues.

Solid rocket propellants containing AP/aluminum are not useful for the preparation of smokeless formulations due to the development of hydrochloric acid and/or solid particles of aluminum oxide during combustion. In order to achieve smokeless propulsion, the perchlorate oxidizer and aluminum fuel may be replaced by nitramines such as RDX or HMX. Due to the slightly negative oxygen balance of these nitramines, such propellant formulations necessitate the use of energetic binders (e.g. GAP, polyBAMO, polyAMMO, polyNiMMO etc.), frequently in combination with energetic plasticizers (e.g. TMETN, BuNENA etc.), in order to obtain a satisfactory oxygen balance and sufficiently high specific impulse.

The introduction of nitramines as well as energetic binder systems complicates the adhesion issues of particles and binder matrix in composite rocket propellants considerably [8-10]. Energetic binders and plasticizers, unlike the standard polybutadiene systems, are polar compounds with heightened surface energies and an enhanced solubilizing power for polar compounds like fillers, bonding agents etc. In addition, energetic binder systems are in general heavily plasticized, which in turn adds to the heightened solubility issues. Liquid polar bonding agents like Tepanol are thus more readily and often fully dissolved into the binder matrix, potentially making adhesion to particle surfaces more difficult than in nonpolar systems. However, the use of polar bonding agents like Tepanol in an energetic binder like GAP is still possible if particles of AP are incorporated as the cation exchange reaction of AP and Tepanol can distort the solubility equilibrium and still secure at least some level of adhesion of the bonding agent. However, the incorporation of nitramines like RDX or HMX is more problematic as the surface of nitramine crystals is chemically unreactive towards common propellant components, making specific covalent interactions between nitramine particles and bonding agent much more difficult or even nonexistent. Therefore, such propellant systems with traditional bonding agents in general tend to have poor mechanical properties.

In order to overcome adhesion issues in nitramine-based smokeless propellants, two general lines of research have been pursued [8-15]. The first of these is a precoating procedure where the nitramine particles are precoated in a separate step prior to the propellant preparation [11-13]. Such coatings should fully cover the nitramine particles with a highly crosslinked and tough polymer shell that enhance adhesion to the binder matrix relative to the nitramine surface alone. Allen published a precoating of HMX in the early 1980s based on water soluble animal protein (collagen) [11], and in the late 1990s, Oberth developed a polyurea coating to tackle the same issue in nitramine propellants [12]. Both of these procedures are essentially based on the assumption that these tough polyamide type coatings can, unlike the nitramine surface alone, bind covalently to the binder during cure. While such precoating procedures evidently do provide enhanced adhesion of the nitramine particles and elastomer matrix, they are nevertheless unpractical as a separate and additional processing step (the precoating) for the major constituent of the propellant (the nitramine) is required [11-13].

The other line of research for enhanced mechanical properties of smokeless propellant formulations is based on the classical bonding agent approach detailed above, in an attempt to overcome the limitations posed by traditional bonding agents in these polar propellant systems. Bonding agents for nitramine propellants, based on amide compounds like hydantoins and isocyanurates have been proposed by Consaga since the mid 1970s [14,15]. Other bonding agents have also been proposed [16], but they all suffer from the fact that they are designed for systems with relatively nonpolar binder systems like polybutadiene, thereby circumventing the problems associated with the introduction of energetic binders/plasticizers needed in smokeless formulations as outlined previously.

The most useful and general approach to improve filler-matrix adhesion in nitramine propellants with energetic binder systems is the family of neutral polymeric bonding agents (NPBA) introduced by Kim in the late 1980s [8-10]. By introducing a macromolecular bonding agent, it is possible to create a polar bonding agent with a favourable adsorption onto the nitramine surface while still having suitable solubility in the polar matrix to allow processing, but avoid full dissolution into the binder system during curing. Reactive pendant hydroxyl functionalities are incorporated through copolymerization, and the assumption is that these react with isocyanate curing agent (both for crosslinking and binder attachment) and are crucial for function. Herein, we describe our research and development with such neutral polymeric bonding agents based on acrylonitrile (both new and previously reported), their detailed characterization and use in smokeless propellant formulations based on HMX, GAP and BuNENA. Finally, we relatively briefly discuss some aspects of their characteristics and possible mode of action.

## 2 Experimental

### 2.1 Chemicals

GAP diol prepolymer ( $M_n = 1750$ ,  $M_w = 1950$ , equivalent weight 1320) was acquired from Eurenco (France), the curing agent Desmodur N100 from Bayer MaterialScience (Germany), the plasticizer BuNENA and HMX from Chemring Nobel AS (Norway), and the curing catalyst TPB from Apros Corporation (South Korea). The polyethylene glycol (PEG) – polypropylene glycol (PPG) polyether polyol (Voranol) was obtained from Dow Chemical. All reagents and solvents

for synthesis of NPBA were acquired from Sigma-Aldrich and used without further purification. Two HMX particle size fractions (50-60  $\mu\text{m}$  and 4-5  $\mu\text{m}$ ) were used for the propellant formulations (Table 1).

## 2.2 Instruments and Analysis

Propellant mixtures were prepared in an IKA vertical mixing system HKV-1 and mechanical tensile testing was conducted with an 810 MTS (Material Testing System) according to the procedure of STANAG 4506. Thermogravimetric analysis (TGA) was conducted using a TA Instruments TGA 2950 HR, 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. The microscope used for taking pictures is a Zeiss Axio Imager.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance AV-600 spectrometer operating at 600 MHz ( $^1\text{H}$ ) and 150 MHz ( $^{13}\text{C}$ ). Chemical shifts are reported in parts per million ( $\delta$ ) and are reported relative to internal reference of the solvent: 2.49/39.5 for DMSO- $d_6$ . Elemental analyses (CHN and S) were carried out by Mikro Kemi AB in Uppsala, Sweden. Gel-permeation chromatography (GPC) was conducted by Polymer Standards Service (PSS) in Mainz, Germany, using either polymethylmethacrylate (PMMA) or polystyrene (PS) calibration standards and DMF/0.01 M LiBr as solvent.

## 2.3 Synthesis of Neutral Polymeric Bonding Agents

A standard NPBA was synthesized in analogy with the literature procedure [10]: A 250 mL round bottom flask was charged with a solution of azobisisobutyronitrile (AIBN, 3.00 g, 18.3 mmol) in a mixture of acrylonitrile (53.08 g, 1.00 mol), 2-hydroxyethyl acrylate (23.29 g, 0.20 mol), methyl acrylate (25.84 g, 0.30 mol) and 2-mercaptoethanol (3.92 g, 50.2 mmol), followed by acetone (125 mL). The solution was heated to 60 °C and magnetically stirred for 6 h. The viscous solution was then allowed to reach room temperature and was poured into methanol (1250 mL). The mixture was stirred and allowed to settle for 10 min. The supernatant was decanted and more methanol (500 mL) was added. The mixture was stirred, left for 10 min and then decanted. More methanol (500 mL) was added and the mixture was left overnight (16 h). The supernatant was decanted, and a final portion of methanol (250 mL) was added and then decanted after stirring and subsequent settling for 10 min. The polymer was dried under high vacuum at room temperature for 24 h to yield the NPBA (89.54 g, 88% yield based on recovery of monomers) as a brittle solid polymer. The polymer was ground in a mortar with pestle to a fine white powder and homogenized by tumbling prior to analysis and use in propellant formulations. It was stored refrigerated to avoid agglomeration. Element analysis (%): C = 59.85, H = 6.55, N = 12.95, S = 1.15. GPC analysis (DMF/0.01 M LiBr, PMMA calibration):  $M_n$  = 4330,  $M_w$  = 8840, PDI = 2.04. GPC analysis (DMF/0.01 M LiBr, PS calibration):  $M_n$  = 4590,  $M_w$  = 9430, PDI = 2.05.  $^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ ):  $\delta$  = 4.73-4.86 (m, OH), 3.98-4.17 (m,  $\text{CO}_2\text{CH}_2$ ), 3.48-3.71 (m,  $\text{CH}_3$ ,  $\text{CH}_2\text{OH}$ ), 2.38-3.27 (m, backbond CH), 1.52-2.20 (m, backbond  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (600 MHz, DMSO- $d_6$ ):  $\delta$  = 172.8-174.1 (C=O), 120.0-120.5 (CN), 66.0-66.4 ( $\text{OCH}_2$ ), 58.9-59.0

(CH<sub>2</sub>OH or CH<sub>3</sub>), 51.9-52.0 (CH<sub>3</sub> or CH<sub>2</sub>OH), 41.0 (backbond CH), 34.3-34.6 (backbond CH), 32.5-33.6 (backbond CH<sub>2</sub>), 27.4-27.9 (backbond CH). IR (cm<sup>-1</sup>): 3506, 2953, 2242, 1725, 1449, 1166, 1073, 890, 834, 755.

An analogous methyl ether capped NPBA based on acrylonitrile, methyl acrylate and 2-methoxyethyl acrylate (in the same molar ratios as for the NPBA above) was prepared in complete analogy, but on only 1/5<sup>th</sup> of the scale used above. GPC analysis (DMF/0.01 M LiBr, PMMA calibration):  $M_n = 4790$ ,  $M_w = 8690$ , PDI = 1.81.

## 2.4 Preparation of Composite Rocket Propellants

A detailed propellant composition is provided in Table 1. The NPBA was allowed to dissolve in BuNENA over night at 60 °C before mixing and the HMX was dried at 60 °C for a minimum of 72 h prior to use. The HMX particles were dispersed in a submix consisting of GAP (with the polyether chain extender), BuNENA, NPBA and other minor components and stirred at 55 °C. The curing agent (Desmodur N100) and curing catalyst (TPB) were subsequently added and the mixture was casted under vacuum degassing. The casted propellant was cured at 60 °C for 120 h. The cure ratio of NCO/OH = 1.0 has been used consistently for curing of all propellant formulations reported in this work.

<tabr1>

## 3 Results and Discussion

### 3.1 Synthesis and Characterization of Neutral Polymeric Bonding Agents

In analogy with the reported procedure [10], we prepared two neutral polymeric bonding agents using free radical polymerization in acetone using 2-mercaptoethanol as chain transfer agent (Scheme 1). The first one was the traditional NPBA based on acrylonitrile, 2-hydroxyethyl acrylate and methyl acrylate in a 1:0.2:0.3 molar ratio, exactly as reported by Kim [10]. The NPBA was obtained after precipitation in MeOH and subsequent drying under vacuum as a brittle and glassy polymer, and it should be stored refrigerated (~5 °C) to avoid agglomeration over time. Element analysis of the material gave values completely in line with what was to be expected if the three constituent monomers were incorporated in accordance with the initial monomeric ratios. However, taking into account the substantial quantities of free radical initiator and chain transfer agent utilized in these procedures, we were surprised to observe the rather high molecular weights (approximately 50 000) that were reported for this material in literature [10]. Our own GPC analysis of the material performed by Polymer Standard Service in Germany gave  $M_n = 4330$  and  $M_w = 8840$  (PDI = 2.04) when using PMMA calibration, significantly below reported values but probably more in line with our expectations. Since the reported analyses uses PS calibration standards, an additional GPC analysis using PS calibration was undertaken. It gave insignificant variation relative to the analysis with PMMA calibration ( $M_n = 4590$ ,  $M_w = 9430$ , PDI = 2.05). A second and completely analogous synthesis of the same copolymer and subsequent GPC analysis (using PMMA calibration) gave similar values of  $M_n = 5270$  and  $M_w = 10 100$  (PDI = 1.91). As such, the NPBAs prepared according to these procedures have lower

molecular weights than previously expected, an important fact to keep in mind when analyzing their mode of action. In addition, DSC analysis of NPBA samples showed some degree of foaming taking place at approximately 100 °C, something that may indicate the presence of some residual AIBN initiator in the material.

<scheme1>

In an effort to obtain the same copolymers with a lower polydispersity index, we also investigated reversible addition-fragmentation chain transfer (RAFT) polymerization, a controlled radical polymerization [17]. After some initial trials using a RAFT procedure actually developed for homopolymerization of acrylonitrile [18], we successfully copolymerized acrylonitrile, 2-hydroxyethyl acrylate and methyl acrylate in ethylene carbonate with AIBN as radical initiator and 2-cyano-2-propyl benzodithioate as RAFT agent. Successful RAFT polymerization required strictly inert conditions, using predried glassware cooled under argon atmosphere, thoroughly degassed solvent and argon atmosphere during all transfers and reaction. Depending on initiator and RAFT agent concentration, we obtained number average molecular weights ( $M_n$ ) ranging from approximately 7000 to 15 000 and polydispersity indices in the range of 1.4 to 1.7, lower than free radical polymerization, but rather poor for a controlled radical polymerization. In the end, we did not find the moderate improvements by introduction of RAFT methodology worthwhile, taking into account the cumbersome preparative procedures and the limited scale achievable.

In order to investigate to what extent pendant hydroxyl functionalities, which are incorporated in all reported NPBA by the use of 2-hydroxyethyl acrylate, actually were vital for their successful operation in composite propellants, we prepared a second methyl ether modified NPBA by substituting the 2-hydroxyethyl acrylate with an equimolar amount of 2-methoxyethyl acrylate (Scheme 1). This NPBA-OMe was prepared under the same conditions as the conventional NPBA, and GPC analysis using PMMA calibration again provided the same rather low molecular weights ( $M_n = 4790$ ,  $M_w = 8690$ , PDI = 1.82) as our two samples of conventional NPBA.

### 3.2 Mechanical Properties of Smokeless Propellants Based on HMX-GAP-BuNENA

Neutral polymeric bonding agents are designed for use in energetic binder systems [8-10], and in order to probe how the incorporation of them would influence the mechanical properties of composite propellants, we selected a smokeless formulation based on HMX with GAP-BuNENA as energetic binder/plasticizer (Table 1). As the exact nature of the binder system will influence the exact choice of NPBA composition due to solubility issues, the use of GAP-BuNENA binder system necessitated the use of NPBA that contained methyl acrylate. Although NPBA based solely on acrylonitrile and 2-hydroxyethyl acrylate are useful for other binder systems, we found the heightened solubility provided by incorporation of methyl acrylate useful for the GAP-BuNENA binder system.

Several isocyanate cured propellant formulations based on HMX-GAP-BuNENA with 60% solid loading were prepared (Table 1), using NPBA in amounts ranging from none to 0.20 wt% relative to the overall propellant. All propellant mixtures were undertaken on a 500 g scale

and specimens were prepared for tensile testing. The mechanical properties evaluated from stress-strain curves at room temperature are summarized in Figure 1 and Table 2.

<figr1>

<tabr2>

The addition of NPBA during propellant mixing affected the viscosity of the mixtures to a considerable extent. The NPBA is soluble in the BuNENA plasticizer at 60 °C and was dissolved on beforehand. Upon addition of the NPBA and HMX, the mixture thickened substantially as compared to the same mixture without NPBA. Some rheological data are given in Table 2.

As can be readily extracted from the results in Figure 1 and Table 2, the use of NPBA significantly improves both the tensile strength and elastic modulus of the composite propellants, while the elongation at break is somewhat lowered. It is surprising to see that incorporation of as little as 0.001 wt% of NPBA relative to the propellant still had a clearly detectable effect on the mechanical properties. Use of 0.05 wt% roughly doubled the maximum tensile strength and elastic modulus of the propellant compared to propellant without any NPBA. Due to the marked viscosity increase during propellant preparation when using NPBA, we found it difficult to incorporate larger amounts than about 0.20 wt%. In addition, but probably more so at high NPBA loadings, the cured propellant could form trapped bubbles or nodules, and the tensile specimens tended to rupture in these imperfections during mechanical testing. In general, we found incorporation of NPBA in the range 0.02 to 0.05 wt% the most appropriate and useful in these propellants with a 60% solid loading. Importantly, this is significantly lower than normal monomeric bonding agents which tend to be utilized at approximately 0.1 to 0.2 wt% [1].

Perhaps the most surprising and novel results to be found in Figure 1 and Table 2 are the mechanical properties of the composite propellant using the methyl ether modified NPBA where 2-hydroxyethyl acrylate has been substituted with an equimolar amount of 2-methoxyethyl acrylate. From the existing literature on NPBA, the necessity of the presence of reactive hydroxyl groups in the NPBA for reaction with isocyanate during curing is judged imperative [8-10]. However, propellant containing 0.05 wt% of methyl ether modified NPBA showed almost exactly the same level of mechanical improvement as propellant specimens containing 0.05 wt% of standard NPBA with pendant hydroxyl functionalities, both with regards to maximum strength, elongation or elastic modulus. Accordingly, the widely assumed and critical role attributed to the reaction of hydroxyl functionalities in the NPBA and isocyanate curing agent in the binder system may perhaps be overestimated. However, also NPBA-OMe does contain reactive hydroxyl groups due to the chain transfer and termination reactions occurring during preparation as 2-mercaptoethanol becomes incorporated at the end(s) of the polymer chains. We will comment more fully on the implications of this in our discussion in the final section.

We also investigated the mechanical properties of our composite propellants containing NPBA at lower temperatures. At NAMMO Raufoss, a 3.5 kg batch of identical HMX-GAP-BuNENA propellant with 60% solid loading and 0.02 wt% of standard hydroxyl-containing NPBA was prepared in complete analogy with our procedures at FFI. Propellant specimens for tensile testing were prepared and the results from the mechanical testing conducted at 21 °C, -25 °C and -40 °C respectively are presented in Figure 2 and Table 3.

<figr2>

<tabr3>

Generally, movement of polymer chains relative to one another is curtailed at low temperatures and accordingly, the elastic modulus and tensile strength increase while elongation at break decreases for most polymeric materials as temperatures are lowered. From the data presented in Table 3 and Figure 2, propellant tensile strength as well as elastic modulus increase as the temperature is lowered and the composite becomes stiffer and stronger. However, when cooling from room temperature to -25 °C and -40 °C, the stress-strain curves for the elastomer composite show a transition from a homogeneous (neckless) stretching into an inhomogeneous stretching with a characteristic necking (“knee”) and pronounced ductile behavior, actually resulting in an increased overall elongation at break at lower temperatures when compared to room temperature. This increased elongation at low temperature is not unique for these propellants, and it can also be observed for nitrate ester polyether/ester (NEPE) propellants [19]. The suggested explanation for this behavior in NEPE propellants is linked to strain induced crystallization [19].

The yield behavior (tensile deformation) of polymers can vary substantially according to both polymer type and temperature, and adhesion issues in a composite elastomer complicate matters even further. Generally, as found for both glass-like and crystalline non-crosslinked polymers, the yield behavior undergoes a transition from a homogeneous and neckless stretching at higher temperatures into an inhomogeneous stretching with necking at lower temperatures [20]. However, for non-crystallizable elastomers above their glass transition temperature, cold drawing is rarely observed. On the other hand, cold drawing can be seen for semicrystalline elastomers like those containing liquid crystalline domains [21]. Therefore, for the highly polar GAP-BuNENA binder system present in these propellant composites, the binder system may perhaps exhibit semicrystalline behavior at low temperatures, resulting in necking, cold drawing and subsequently an increased elongation in the ductile region as strongly interacting polymer chains align themselves through the viscous flow during cold drawing. Tendencies to strain induced crystallization will obviously increase this effect. Strain induced crystallization tends to take effect primarily at high elongations, typically several hundred percent for natural rubber [22,23]. In any effect, there are reasons to believe that the regular chemical structure of GAP polymer chains coupled with its strong polar intermolecular interactions gives rise to semicrystalline behavior, e.g. strain induced crystallization, when approaching the glass transition temperature of the binder system, something that may account for GAP’s interesting low temperature properties. However, there is much that remains to be understood concerning the low temperature behavior of these energetic binder systems.

The apparent inhomogeneous stretching observed for these propellant composites at low temperatures complicates the analysis of interfacial interaction between HMX particles and the GAP rubber matrix as adhesion issues and semicrystalline behavior of the elastomer matrix can be intertwined. We therefore undertook dynamic mechanical analysis (DMA) of six propellant samples, one sample without NPBA and five samples containing different concentrations of NPBA, at -60 °C to 0 °C to probe the interfacial interaction between GAP and HMX in our composite propellants. Results in the most relevant temperature region (-25 to -50 °C) are presented in Figure 3.



<figr3>

In Figure 3, the damping factor (tangent delta) is plotted as a function of temperature for the different propellant composites. As the damping factor is the ratio of the loss (viscous) modulus to the storage (elastic) modulus, greater damping is an indication of reduced elastic response and increased dissipative energy losses due to viscous flow. Decreased damping is therefore an indication of improved filler-binder interactions [24]. The general trend readily extracted from Figure 3 is that the damping noticeably decreases with increasing concentrations of NPBA in the low temperature region where definitive analysis is possible, clearly manifesting that NPBA raises adhesion of the GAP binder and HMX filler and imparts improved elasticity in the composite propellants. At higher temperatures, only modest differences in the damping factor can be observed among the various propellant specimens, but the improved adhesion using NPBA is of course still apparent during tensile testing as both tensile strength and modulus increase.

During propellant curing, IR was performed on samples both with and without NPBA. No noteworthy differences in curing rate could be detected, indicating that the use of NPBA will neither affect the curing rate nor pot life of the propellant to any appreciable extent. In order to access where and how the NPBA ended up in the cured propellant samples, we studied the different samples thoroughly by microscopy, using both an optical microscope and a scanning electron microscope (SEM). The distribution of NPBA seemed to some extent to be correlated according to its concentration range. By our investigations at least, we did not find any particular indication that crystals of HMX were fully enveloped in tough coatings of NPBA, at least at low NPBA loadings. Needle tests also indicated a noticeably poorer bonding of the nitramine particles in the binder matrix as when compared to AP crystals in a standard HTPB matrix with Tepanol as bonding agent.

Figures 4-6 show pictures of the fracture surfaces of three different propellant specimens containing no NPBA (Figure 4), 0.05 wt% of NPBA (Figure 5) and 0.20 wt% of NPBA (Figure 6) after tensile testing. As can be clearly seen, propellant without NPBA has a distinctly poor adhesion of nitramine filler and binder matrix with no apparent inhomogeneities in the binder or HMX distribution (Figure 4). Propellant samples containing approximately 0.02 to 0.05 wt% NPBA contained relatively heterogeneously distributed NPBA, the specimens containing some characteristic clusters of what appears to be heteroagglomerated HMX probably containing NPBA, something that may indicate some bridging type effect that give rise to these small HMX agglomerates. The fracture surfaces of the same samples (Figure 5) could also contain distinctive thin threads after mechanical testing. Propellant specimens containing larger quantities of NPBA (0.10 to 0.20 wt%) did not form threads at the fracture surfaces after mechanical testing and seemed to have a significantly stronger binder-filler adhesion and more homogeneously distributed NPBA (Figure 6), appearing much more like samples of AP propellants with Tepanol bonding agent than the other propellant samples. The sample containing the NPBA-OMe looked indistinguishable to an analogous sample with standard NPBA. However, it should be stressed that these fracture surfaces can vary substantially from sample to sample and that the trends outlined should be understood as only indicative and subsequently be treated with great caution. Varying elongation prior to eventual sample fracture during tensile testing of the various propellant specimens will also influence the character of the fracture surfaces.

<figr4>

<figr5>

<figr6>

At least to the extent that it could be established, we did not find the HMX in our propellant samples to contain tough crosslinked coatings of NPBA. Interactions of the bonding agent with the HMX filler surfaces are presumably noncovalent by nature. This is probable as the interactions of the Lewis basic nitrile groups of the NPBA and the strongly Lewis acidic surface of the HMX filler would be noncovalent. Strong noncovalent interactions could also explain the significant increase in viscosity during propellant processing that is associated with the presence of NPBA in the propellant mixture. During processing, it looked as if the NPBA underwent phase separation to some extent when all GAP had been added and that it was kneaded mechanically into the propellant mixture upon addition of HMX.

As for GAP-NPBA interactions, azide groups may undergo thermal cycloaddition with nitriles to form tetrazoles under forcing conditions [25], and we carried out a separate experiment to ascertain whether this was likely to occur under propellant cure, even though it was known from previous literature that NPBA are effective in azide-free binder systems as well [8,9]. A sample of GAP was mixed with adiponitrile and placed in a rheometer at 60 °C. Even after 80 h, no apparent crosslinking by tetrazole formation and subsequent increase of viscosity could be detected. The interactions of the NPBA towards isocyanates the binder system will be discussed in the final section.

### 3.3 Ballistic Properties of Smokeless Propellants Based on HMX-GAP-BuNENA

Achieving minimum smoke or near smokeless rocket propulsion is the main incentive for the interests surrounding the use of nitramine based propellant formulations with energetic binder systems. The use of energetic binder systems is partially necessitated due to the slightly negative oxygen balance of HMX or RDX. The use and understanding of NPBA are therefore intrinsically connected with minimum smoke formulations and consequently of the highest relevance in current rocketry.

The theoretical specific impulse and characteristic exhaust velocity of the HMX-GAP-BuNENA formulation at 60% solid loading described herein were calculated using the Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications from NASA [26]. From the 3.5 kg propellant batch prepared at NAMMO Raufoss, three 2" ballistic evaluation rocket motors were cast and relevant ballistic properties such as burning rate and pressure index were determined by static testing using three different nozzle sizes. All the ballistic data are presented in Table 4. The propellant does not contain burning rate catalysts.

<tabr4>

As we are mainly concerned with the mechanical properties of the propellant in this work, we use a relatively low 60% solid loading to ensure successful processing when using the polymeric bonding agents. As such, the specific impulse of the propellant is rather moderate, but ballistic performance will be studied and improved more extensively at a later stage.

### 3.4 Mechanism of Action of Neutral Polymeric Bonding Agents

We will continue in this final section with some remarks concerning possible mode of action for neutral polymeric bonding agents, strengthening the analysis with some of our experimental results. The discussion will certainly be incomplete as our current understanding of the mode of action for neutral polymeric bonding agents is only partial. Issues concerning dewetting and binder-filler interactions for nitramines have been discussed for decades in the literature [16], above all because of the unreactive nature of nitramine surfaces [27]. The introduction of NPBA has opened up entirely new possibilities and has a distinct economic advantage over precoating procedures. In existing literature, it is explicitly stated and verified experimentally that the effect of NPBA incorporation is interfacial and not due to an overall increase in crosslink density of the binder [9]. It was also directly demonstrated that NPBA had a favorable relative affinity to HMX and concentrated at the solid surface during mixing by studying adsorption of NPBA onto HMX from a solution of NPBA in TEGDN [9]. The preparation of NPBA does not involve the use of acidic or basic constituents so as to avoid any compatibility issues with the nitramines, energetic binders or nitrate ester plasticizers, hence their name neutral polymeric bonding agents.

First, we would like to provide a precautionary note based on the fact that previous literature on mechanism of action of NPBA is based mainly on HMX-PEG propellants with nitrate ester plasticizers [8,9], while this work is based on HMX-GAP propellants with BuNENA plasticizer, and causal relationships may differ for the two propellant types. Other relevant publications involving use of NPBA exist, but details there are sparse regarding mechanistic insight [28]. The reported HMX-PEG propellant has exceptionally poor mechanical properties in unmodified form, and the use of NPBA offered up to a fivefold increase in tensile strength [8]. Our HMX-GAP propellant has somewhat better mechanical properties in unmodified form, but the use of NPBA still offered an approximately twofold increase in both tensile strength and elastic modulus.

It has been well established that precoating of nitramines can give filler reinforcement and improved mechanical properties [11-13], presumably by covalent shell reinforcement where particles are enveloped in a tough and stiff shell that resist tear [9,29]. In the pioneering work of Kim and coworkers, three paramount characteristics of a successful bonding agent were detailed [8]: 1) It should be accumulated at the surface of the solid filler particles; 2) it should undergo crosslinking reaction with the curing agent to form hard and tough shells around the particles; 3) it should have enough functional groups left to form primary chemical bonds between the shells and the binder network.

As for criteria 1), macromolecules like NPBA are especially useful since they may be much more surface active than small molecules. Macromolecular composition can be tuned so as to match the properties of the filler surface. In a conference proceeding we have published concurrently with this work, we have studied the surface energy of NPBA in detail using contact angle measurements of water and diiodomethane on films of NPBA (deposited from solution) and compared them to the surface energies of RDX, HMX, GAP and BuNENA [30].

Criteria 2) and 3) are solved (at least in theory) by NPBA copolymerization including 2-hydroxyethyl acrylate to give a polymer with pendant hydroxyl groups for crosslinking with isocyanate and binder attachment. We found our NPBA-OMe to improve the mechanical properties of the cured propellant to more or less the same extent as standard NPBA, something that is somewhat at odds with the formation of extensively isocyanate crosslinked tough shells

surrounding the HMX particles. However, as we pointed out earlier, even the NPBA-OMe contains reactive functionalities as 2-mercaptoethanol is incorporated by chain transfer and termination reactions during preparation. Indeed, separate experiments verified that solutions of either NPBA or NPBA-OMe in an organic solvent like DMF can both be rapidly coagulated by addition of a solution of methylene diphenyl diisocyanate (MDI) in DMF. Sulfur analysis of our standard NPBA gave a value of S = 1.15% (see experimental section), something corresponding to ca. 0.36 mmol mercaptoethanol-originated moiety per gram NPBA. This does not take into account other reactive functionalities that may result from side reactions during synthesis.

Work to be published later by us on isocyanate-free curing systems for GAP has conclusively shown that NPBA does not function properly in curing systems devoid of isocyanates. Subsequently, at this point we believe reactive functionalities in the NPBA to be vital for adhesion and linkage to the binder system, but probably less so for crosslinking.

Finally, it is noticeable how NPBA is capable of improving certain mechanical properties of composite propellants, in addition to the increase of viscosity during preparation, even at exceedingly small concentrations. Levels of NPBA as low as 0.001 to 0.005 wt% have a clearly noticeable effect, values far below where all solid particles have full coverage and function fully according to a covalent shell reinforcement effect. We will here avoid the temptation to claim decisive evidence in favor of any particular mode of action for the NPBA class of bonding agents, and we hope it can be unambiguously resolved during future investigations.

## 4 Conclusions

The use of NPBA significantly enhances the tensile strength as well as the elastic modulus of isocyanate cured HMX-GAP-BuNENA composite propellants, roughly doubling both relative to NPBA-free propellant at 0.02 wt% of NPBA. Dynamic mechanical analysis of propellant specimens clearly indicated an improved binder-filler interfacial interaction in the propellant composites containing NPBA relative to propellant without any NPBA, and the adhesion improved with increasing amounts of NPBA. NPBA containing a strongly reduced number of reactive hydroxyl groups, made by substituting 2-hydroxyethyl acrylate with 2-methoxyethyl acrylate during polymerization, offered the same level of mechanical improvement as conventional NPBA. However, the presence of some reactive functionalities towards isocyanate curing agents is vital for function.

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### Acknowledgments

We thank NAMMO Raufoss for valuable and friendly collaboration during all parts of this work.

### Symbols and Abbreviations

AIBN	azobisisobutyronitrile
AP	ammonium perchlorate
BuNENA	<i>N</i> -butyl-2-nitratoethylnitramine
Desmodur N100	hexamethylene diisocyanate biuret trimer
DMA	dynamic mechanical analysis
DMF	dimethylformamide
DSC	differential scanning calorimetry
GAP	glycidyl azide polymer
GPC	gel permeation chromatography
HMX	octogen, cyclotetramethylene tetranitramine
HTPB	hydroxyl-terminated polybutadiene
IR	infrared
$M_n$	number average molecular weight
$M_w$	weight average molecular weight
MDI	methylene diphenyl diisocyanate
NEPE	nitrate ester polyether/ester
NMR	nuclear magnetic resonance
NPBA	neutral polymeric bonding agent
PDI	polydispersity index
PEG	polyethylene glycol
PMMA	polymethylmethacrylate
polyAMMO	poly(3-azidomethyl-3-methyloxetane)
polyBAMO	poly(3,3-bis(azidomethyl)oxetane)
polyNiMMO	poly(3-nitratomethyl-3-methyloxetane)
PPG	polypropylene glycol
PS	polystyrene
RAFT	reversible addition-fragmentation chain transfer
RDX	hexogen, cyclotrimethylene trinitramine
SEM	scanning electron microscope
tan $\delta$	tangent delta (tangent of the phase angle)
TEGDN	triethylene glycol dinitrate
Tepanol	tetraethylenepentamine acrylonitrile glycidol adduct
TMETN	trimethylolethane trinitrate
TPB	triphenyl bismuth

## Table Captions

**Table 1.** HMX-GAP-BuNENA smokeless rocket propellant composition.<sup>a)</sup>

Constituent	Percentage [wt%]
HMX (50-60 $\mu\text{m}$ )	38.54
HMX (4-5 $\mu\text{m}$ )	21.46
GAP Diol	21.70
PEG-PPG	3.40
BuNENA	9.54
N100	3.54
TPB	0.02
Stabilizers and minor components	1.80

<sup>a)</sup> In addition, varying amounts of NPBA according to Table 2 was added. Curing ratio NCO/OH = 1.0 and curing time = 120 h at 60 °C for all compositions.

**Table 2.** Tensile testing of HMX-GAP-BuNENA composite propellants with and without NPBA at 21 °C (crosshead speed = 50 mm/min).

NPBA-content [%] <sup>a)</sup>	Max tensile strength [MPa]	Elongation at break [%]	<i>E</i> -modulus [MPa]	Viscosity [Pa·s] <sup>c)</sup>
None	0.33	51.1	2.50	43
0.001	0.42	38.2	3.13	40
0.005	0.46	36.1	3.30	40
0.02	0.58	37.0	4.31	115
0.05	0.64	26.8	4.71	138
0.05 OMe <sup>b)</sup>	0.68	25.2	4.29	123
0.10	0.70	22.6	4.58	435
0.20	0.71	21.3	5.25	n.a.

<sup>a)</sup> Weight% relative to overall propellant. <sup>b)</sup> NPBA with 2-methoxyethyl acrylate. <sup>c)</sup> Magnitude of the complex viscosity of the propellant mixture 1 h after addition of curing agent.

**Table 3.** Tensile testing of HMX-GAP-BuNENA composite propellant with 0.02 wt% NPBA at 21 °C, -25 °C and -40 °C (crosshead speed = 50 mm/min).<sup>a)</sup>

Temperature [°C]	Max tensile strength [MPa]	Elongation at break [%]	<i>E</i> -modulus [MPa]
21	0.58	27.7	4.48
-25	1.24	83.1	5.80
-40	2.29	96.7	17.26

<sup>a)</sup> Mean value of five propellant specimens.

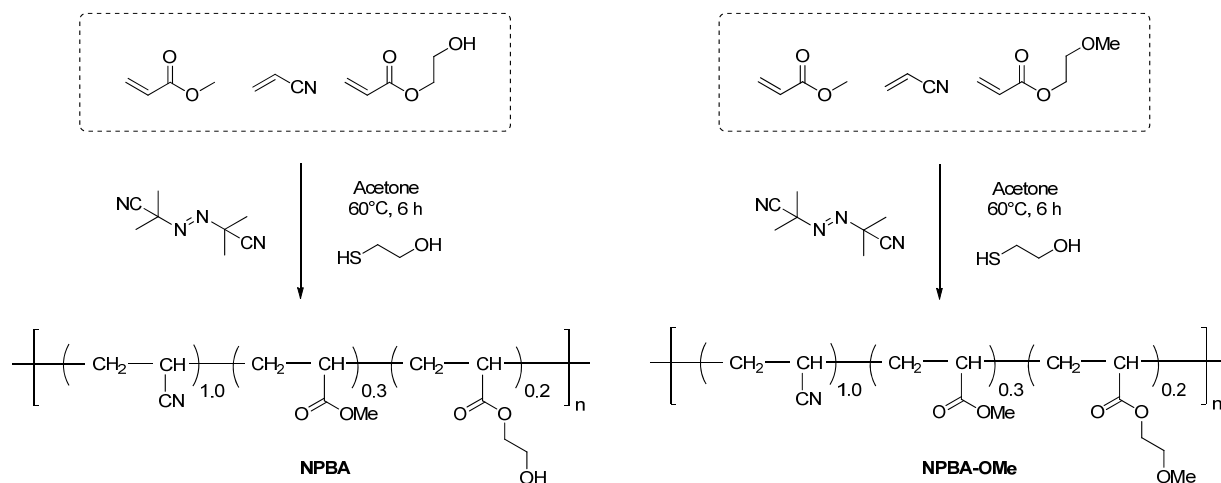
**Table 4.** Ballistic properties of HMX-GAP-BuNENA composite propellant with 60% HMX solid loading.

Ballistic property	Value
Theoretical specific impulse, <sup>a)</sup> $I_{sp}$	2154 Ns/kg
Characteristic exhaust velocity, <sup>a)</sup> $c^*$	1345 m/s
Burning rate at 6.9 MPa <sup>b)</sup>	6.3 mm/s
Burning rate at 10 MPa <sup>b)</sup>	8.1 mm/s
Pressure exponent <sup>b)</sup>	0.66

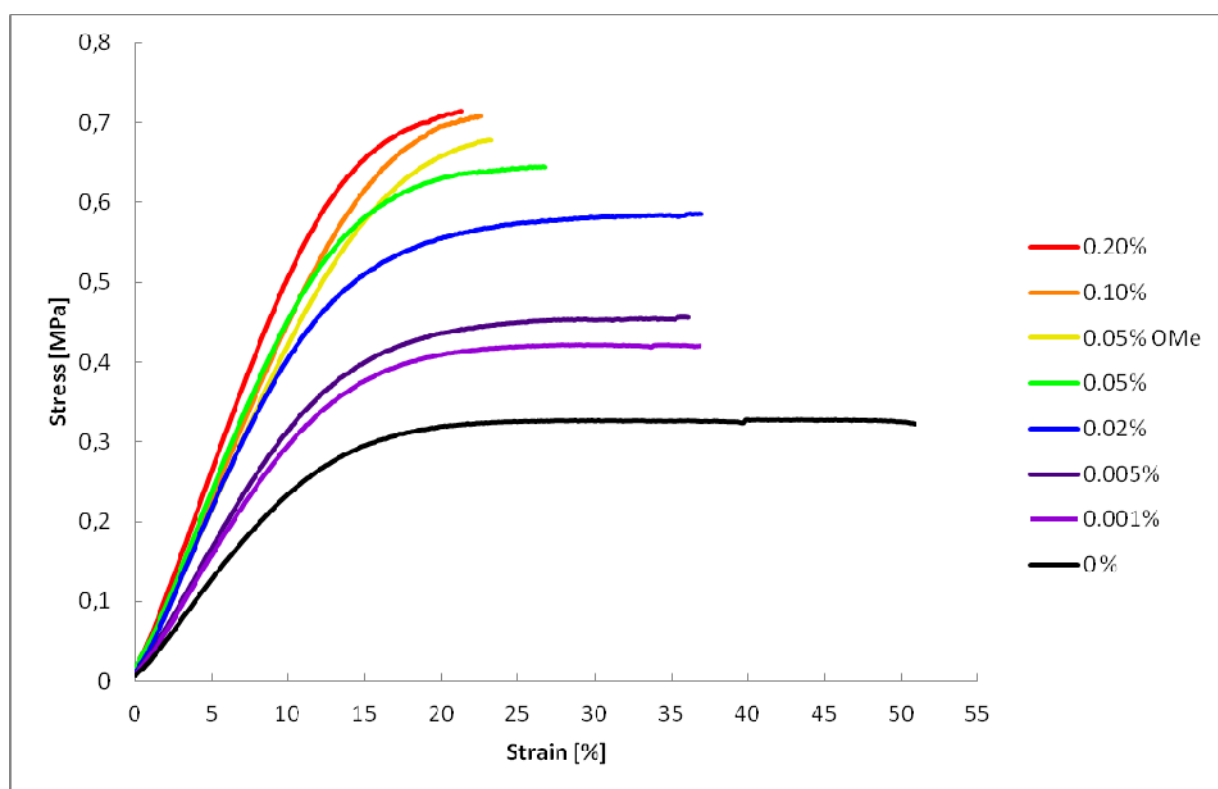
<sup>a)</sup> Calculated with computer software at a chamber pressure = 6.9 MPa and nozzle-expansion ratio = 68.1:1 [26]. <sup>b)</sup> Determined by static testing of three 2” ballistic evaluation rocket motors in the pressure range 8-16 MPa.



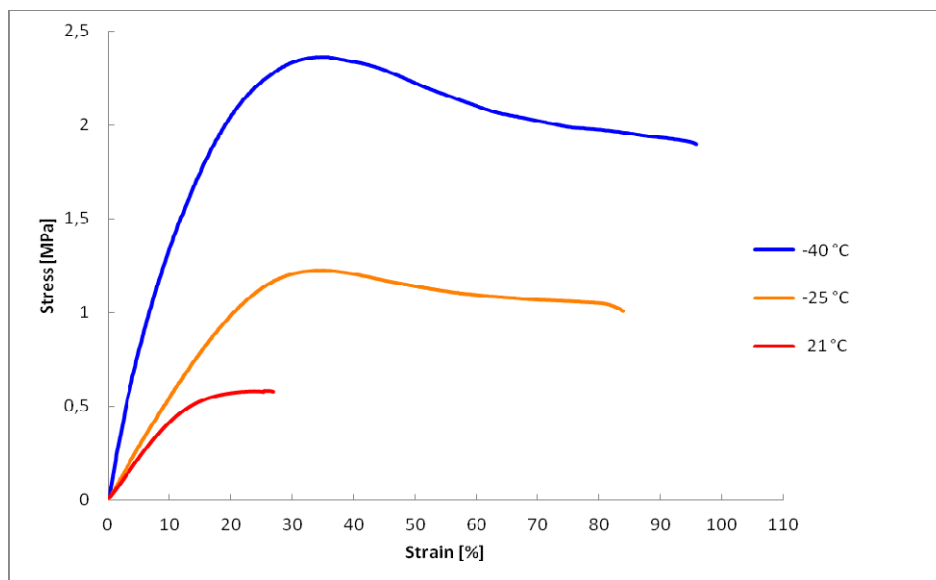
## Scheme and Figure Captions



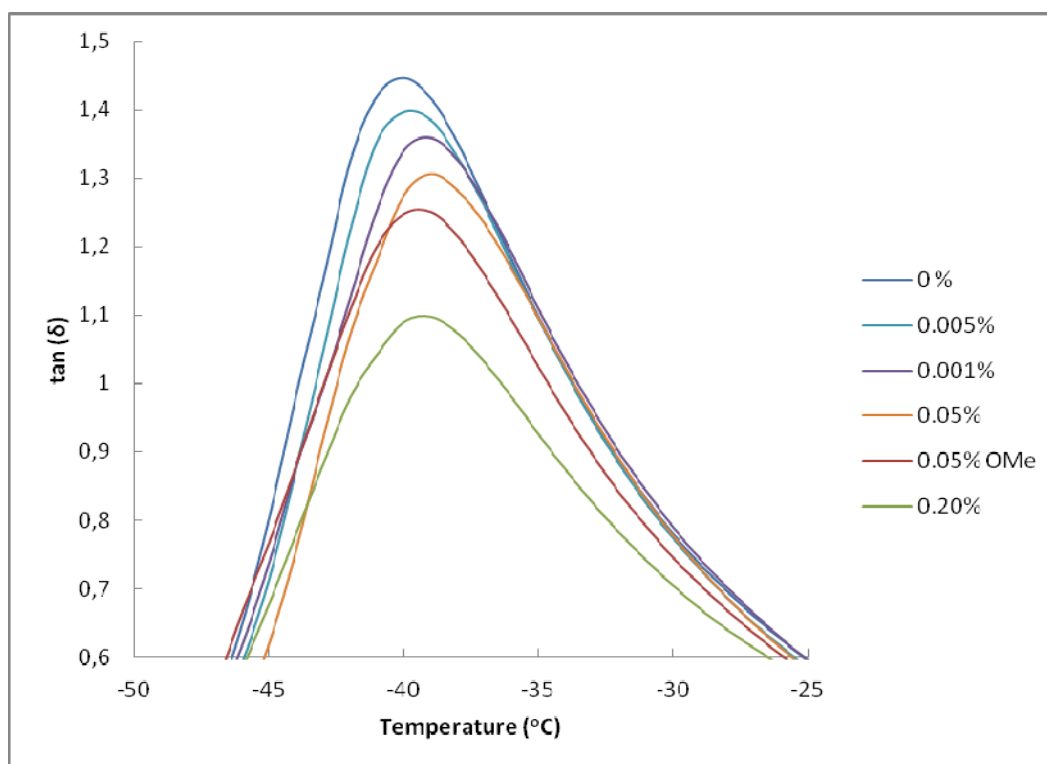
**Scheme 1.** Preparation of Neutral Polymeric Bonding Agents (NPBA and NPBA-OMe) by free radical copolymerization.



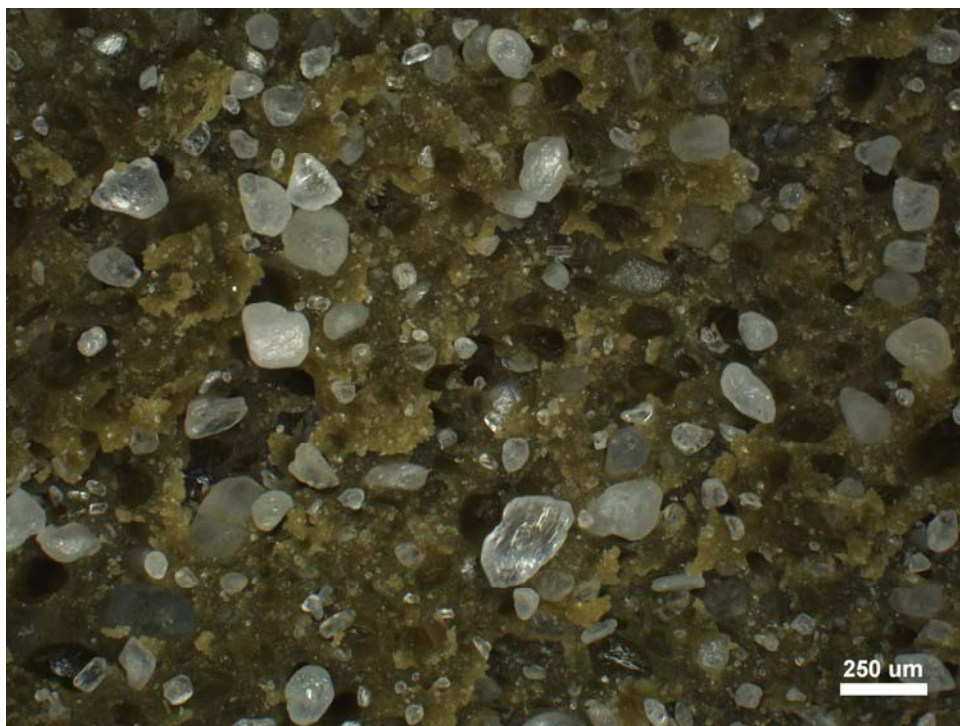
**Figure 1.** Tensile testing of HMX-GAP-BuNENA composite propellants with and without NPBA at 21 °C (crosshead speed = 50 mm/min).



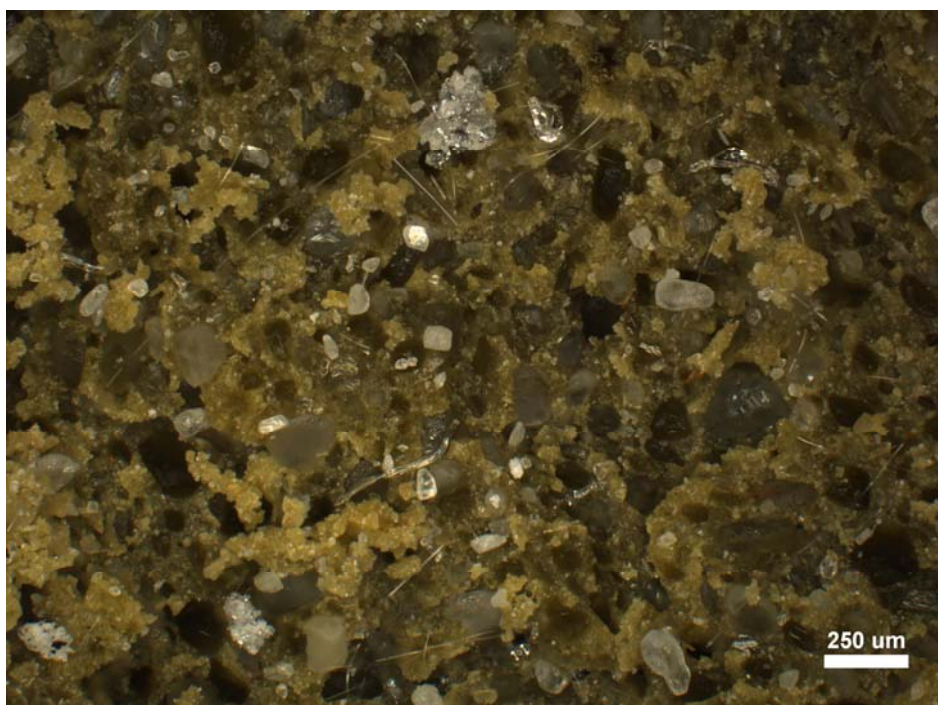
**Figure 2.** Tensile testing of HMX-GAP-BuNENA composite propellant with 0.02 wt% NPBA at 21 °C, -25 °C and -40 °C (crosshead speed = 50 mm/min).



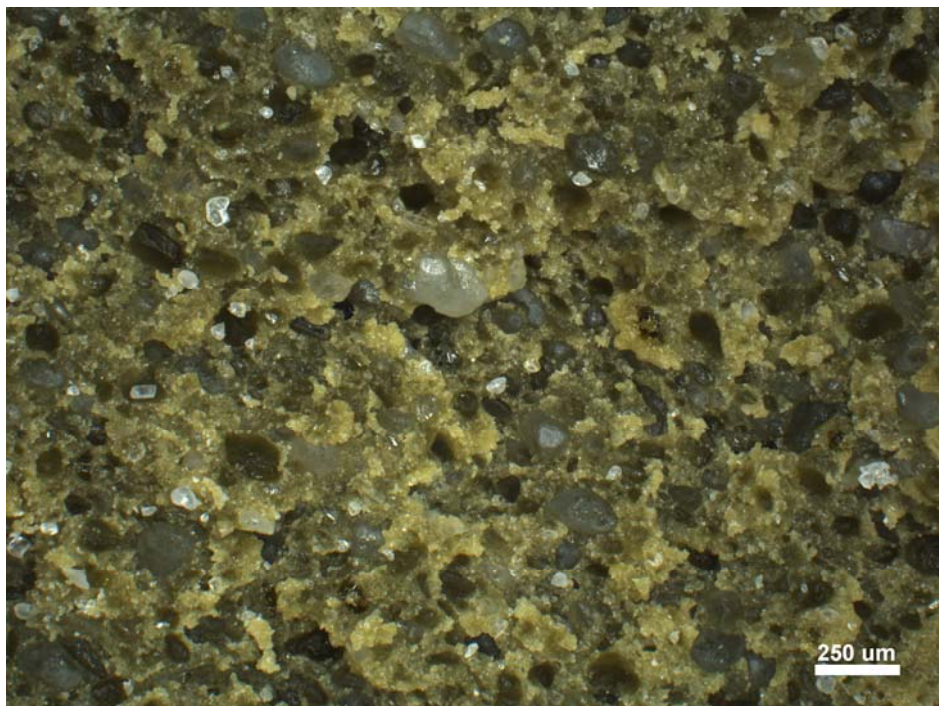
**Figure 3.** Dynamic mechanical analysis of HMX-GAP-BuNENA propellant specimens with and without NPBA (oscillating frequency: 1 Hz, heating rate: 1 K/min, amplitude: 20  $\mu$ m).



**Figure 4.** The fracture surface of HMX-GAP-BuNENA propellant sample with no NPBA after tensile testing.



**Figure 5.** The fracture surface of HMX-GAP-BuNENA propellant with 0.05 wt% NPBA after tensile testing.



**Figure 6.** The fracture surface of HMX-GAP-BuNENA propellant with 0.20 wt% NPBA after tensile testing.