

Isocyanate-Free and Dual Curing of Smokeless Composite Rocket Propellants

Eva Landsem,^[a, b] Tomas L. Jensen,^[a] Tor E. Kristensen,^{*[a]} Finn K. Hansen,^[a, b] Tore Benneche,^[b] and Erik Unneberg^[a]

Abstract: Traditional composite rocket propellants are cured by treatment of hydroxyl-terminated prepolymers with polyfunctional aliphatic isocyanates. For development of smokeless composite propellants containing nitramines and/or ammonium dinitramide (ADN), energetic binder systems using glycidyl azide polymer (GAP) are of particular interest. Polyfunctional alkynes are potential isocyanate-free curing agents for GAP through thermal azide-alkyne cycloaddition and subsequent formation of triazole crosslinkages. Propargyl succinate or closely related aliphatic derivatives have previously been reported for such isocyanate-free curing of GAP. Herein, we present the synthesis and use of a new aromatic alkyne curing agent, the crystalline solid bisphenol A bis(propargyl ether) (BABE), as isocyanate-free curing agent in smokeless propellants based on

GAP, using either octogen (HMX) and/or prilled ADN as energetic filler materials. Thermal and mechanical properties, impact and friction sensitivity and ballistic characteristics were evaluated for these alkyne cured propellants. Improved mechanical properties could be obtained by combining isocyanate and alkyne curing agents (dual curing), a combination that imparted better mechanical properties in the cured propellants than either curing system did individually. The addition of a neutral polymeric bonding agent (NPBA) for improvement of binder-filler interactions was also investigated using tensile testing and dynamic mechanical analysis (DMA). It was verified that the presence of isocyanates is essential for the NPBA to improve the mechanical properties of the propellants, further strengthening the attractiveness of dual cure systems.

Keywords: Propellant · HMX · ADN · GAP · NPBA · Azide-alkyne curing · Isocyanate curing

1 Introduction

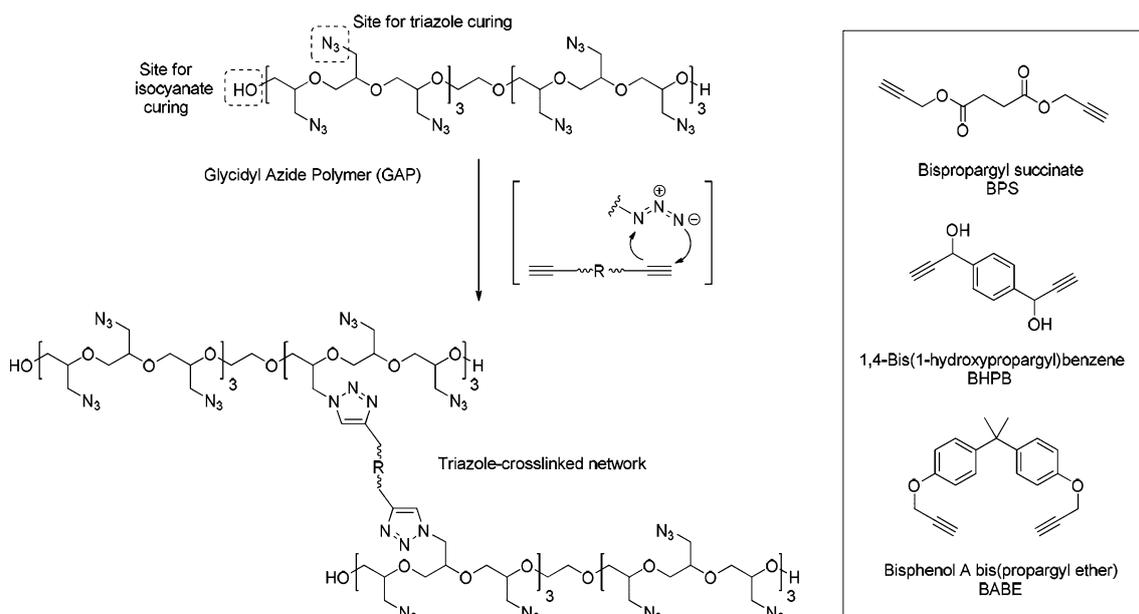
Development of appropriate smokeless composite rocket propellants for replacement of double base formulations is a key area of research within current solid state rocket propulsion. In order to formulate such a propellant, the traditional oxidizer ammonium perchlorate (AP) ought to be replaced with other energetic filler materials due to formation of hydrochloric acid during combustion. Suitable replacements for AP could be nitramines like RDX and HMX or the powerful oxidizer ammonium dinitramide (ADN). Nitramines have high energy content, but due to their slightly negative oxygen balance they cannot contribute oxidatively to the combustion of the binder system. Therefore, it is necessary to replace traditional inert hydroxyl-terminated polybutadiene (HTPB) binder with an energetic binder such as glycidyl azide polymer (GAP) in order to attain satisfactory performance [1]. Hydroxyl-terminated prepolymers are cured with isocyanates, which are compounds that react readily with the hydroxyl groups to form urethane linkages. However, isocyanates are both moisture sensitive and hazardous. In systems containing energetic nitrate ester plasticizers, isocyanates may also lead to the formation of undesired nitroso derivatives, causing degradation of the mechanical properties of the propellant during storage [3]. For these reasons, isocyanate-free

curing systems are of great interest [2–12]. Particularly for ADN, such isocyanate-free curing agents would be very useful due to the severe compatibility issues between ADN and isocyanates [10].

An alternative curing system for GAP binders is founded on the Huisgen thermal cycloaddition reaction [13] of the azide moieties in GAP with polyfunctional alkynes [2–12]. The reaction is a 1,3-dipolar [3 + 2] cycloaddition reaction and forms crosslinkages in the form of aromatic triazoles (Scheme 1). In the thermal non-catalyzed version [13], the triazole formation is not regiospecific, but the analogous and mechanistically distinct cycloaddition catalyzed by Cu^I catalysts results in regiospecific 1,4-triazole formation. The latter reaction, referred to as the Cu^I catalyzed azide-alkyne

[a] E. Landsem, T. L. Jensen, T. E. Kristensen, F. K. Hansen, E. Unneberg
Norwegian Defence Research Establishment (FFI)
P. O. Box 25
2027 Kjeller, Norway
*e-mail: Tor-Erik.Kristensen@ffi.no

[b] E. Landsem, F. K. Hansen, T. Benneche
Department of Chemistry
University of Oslo
P. O. Box 1033
0315 Oslo, Norway



Scheme 1. Reaction scheme for curing of GAP by 1,3-dipolar azide alkyne cycloaddition.

cycloaddition, is widely considered to fall within the “click chemistry” concept proposed by Sharpless [14], and was discovered independently by the research groups of Sharpless [15] and Meldal [16] around 2002. Triazole formation is favored by electron donating groups on the azide and electron withdrawing groups on the alkyne [17]. Some degree of control of the propellant curing rate can therefore be obtained by adjusting the alkyne structure.

Some experimentation on curing of azide prepolymers using dipolarophiles has most probably been undertaken since the 1980s, and curing of GAP with a variety of dipolarophiles, like multifunctional aliphatic acrylates, was patented by Manzara in 1997 [2]. Reed patented the crosslinking of azide polymers (GAP, polyAMMO, polyBAMO etc.) with aromatic diethynylbenzenes in 2000 [3]. In 2005, Ciaramitaro patented the curing of azide prepolymers using tri- or dipropargyl esters of trimesic and/or isophthalic acid, also using ADN as filler material [4]. Since 2008, the curing of azide polymers with GAP has been studied in more detail [5–12], especially by Keicher and co-workers [5–7] and Menke and co-workers [8,9]. Keicher and co-workers have studied the curing of GAP with bispropargyl succinate (BPS) [5–7], easily obtained by the Fischer esterification of succinic acid and propargyl alcohol, and by far the most widely studied isocyanate-free curing agent. Such mixtures can have satisfactory pot lives and curing times, which are important properties for an application like rocket propellant formulation, but exhibited slightly elevated glass transition temperatures compared to isocyanate cured systems. The use of the propargyl ester of 3,6,9-trioxaundecanedioic acid was also investigated [7]. Menke and co-workers have investigated the use of BPS for curing of ADN-GAP propel-

lants, and found that the burning rate was slightly higher than for isocyanate cured propellants [8,9].

Pontius et al. studied heat generation in the curing of GAP with either isocyanates or BPS, and their compatibilities with ADN, in great detail using microcalorimetry [10]. They indicated that contrary to isocyanates, the isocyanate-free curing system was compatible with ADN, thus enabling its use in ADN-based propellants. Swedish researchers have reported the synthesis of an alkyne functionalized and hyperbranched copolymer based on 3-ethyl-3-(hydroxymethyl)oxetane (TMPO) and tetrahydrofuran (THF) and the use of this polymer to cure GAP [11]. Very recently, scientists from the Agency for Defense Development (ADD) in the Republic of Korea published a study on the curing of GAP with BPS, 1,4-bis(1-hydroxypropargyl)benzene (BHPB), mixtures of BPS and BHPB, and a dual curing system composed of mixtures of isocyanate and alkyne [12]. The dual curing system gave improved mechanical properties compared to pure triazole-based curing.

In this work, we report the synthesis and use of a new curing agent, bisphenol A bis(propargyl ether) (BABE), for use in smokeless composite propellants based on GAP with HMX and/or ADN as energetic filler materials. This difunctional propargyl ether, which is a convenient crystalline material, is easily synthesized on large scale from inexpensive and commercially available starting materials. When appropriate energetic plasticizers are used, this propargyl ether also has sufficient solubility in a GAP-binder system to avoid the use of solvents during propellant processing. The motivation for the development of BABE originated from the similarity between this molecule and 4,4'-methylene diphenyl diisocyanate (MDI), an isocyanate curing agent known to impart good mechanical properties in polyur-

ethanes, but which reacts too fast to be utilized in propellant curing processes. The use of Cu^I catalysis during triazole curing was excluded as Cu^I forms a highly sensitive explosive when in contact with dinitramide [11].

2 Experimental Section

2.1 Chemicals

GAP diol prepolymer ($M_n=1750$, $M_w=1950$, equivalent weight 1320) was acquired from Eurenco (France), the isocyanate curing agent hexamethylene diisocyanate biuret trimer (Desmodur N100) from Bayer MaterialScience (Germany), isophorone diisocyanate (Vestanat IPDI) from Evonik Industries, and the curing catalyst triphenyl bismuth (TPB) from Apros Corporation (Republic of Korea). The plasticizer *N*-butyl-2-nitratoethylamine (BuNENA) and HMX were acquired from Chemring Nobel AS (Norway), and the trimethylolethane trinitrate (TMETN) plasticizer from SNPE (France). Prilled ADN was purchased from Eurenco Bofors – FOI. Representative data for prilled ADN: M.p. 92.4 °C, density = 1.796 g cm⁻³, size distribution with 10% below 52 μm, 50% below 195 μm, and 90% below 362 μm. The bonding agent (NPBA-OMe) is a copolymer of acrylonitrile, methyl acrylate, and 2-methoxyethyl acrylate in ratios 1.0:0.3:0.2 and was synthesized as described by us previously [18]. Standard laboratory reagents and solvents were acquired from Sigma-Aldrich and used without further purification.

Two HMX particle size fractions (50–60 μm and 4–5 μm) were used for propellant formulations. The curing ratios NCO/OH and alkyne/GAP used for propellant formulations are given in Table 1, Table 2, and Table 3.

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. Dynamic mechanical analysis (DMA) was performed with a TA Instruments DMA 2980 and differential scanning calorimetry (DSC) was carried out with a TA Instruments DSC Q1000. Rheology properties were measured on a Paar Physica UDS 200 with an 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 (using the average value of the top and bottom of the propellant specimen). IR of pure BABE was recorded with a Bruker Vertex 70 FTIR instrument using Specac GoldenGate with a DLATGS detector.

¹H NMR and ¹³C NMR spectra were recorded with a Bruker AVII 400 spectrometer operating at 400 MHz (¹H) and 100 MHz (¹³C). Chemical shifts are reported in parts per million (δ) and are reported relative to internal reference of

the solvent: 7.27/77.0 for CDCl₃. Elementary analysis was carried out by Eurofins Mikro Kemi AB in Uppsala, Sweden.

2.3 Synthesis and Characterization of Bisphenol A Bis(Propargyl Ether)

Bisphenol A bis(propargyl ether) (BABE) was prepared by a Williamson ether synthesis, founded on a reported procedure [19], and using a modified work-up to avoid a separate recrystallization step: A 1000 mL three-necked round-bottomed flask equipped with mechanical stirring was charged with a solution of potassium hydroxide (86 wt-%, 84.0 g, 1290 mmol) in ethanol (96 vol-%, 300 mL), and the solution was stirred until all potassium hydroxide was dissolved. Bisphenol A (140.1 g, 610 mmol) was added portion wise whilst stirring, followed by an additional quantity of ethanol (96 vol-%, 200 mL). The mixture was stirred to give a transparent solution. Propargyl bromide (80 wt-% in toluene, 150 mL, 1350 mmol) was added via additional funnel over a period of 30 min. The solution was heated to 85 °C and stirred at this temperature for 5 h. Agitation was discontinued and the precipitated potassium bromide was allowed to settle. The hot reaction mixture was filtered, and the residue was washed thoroughly with hot ethanol (96 vol-%, 3 × 200 mL). The filtrate was allowed to cool to room temperature and water (900 mL) was added whilst stirring, causing the reaction product (BABE) to precipitate. The dispersion was stirred for an additional 25 min and further cooled on ice before isolation by vacuum filtration. The product was washed with ethanol (96 vol-%, 3 × 200 mL) and dried at room temperature to give bisphenol A bis(propargyl ether) (155.1 g, 83% yield). M.p. 79–80 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (4 H, aromatic H), 6.90 (4 H, aromatic H), 4.70 (4 H, CH₂), 2.60 (2 H, CH), 1.75 (6 H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 155.6 (aromatic C), 144.0 (aromatic C), 128.0 (aromatic C), 114.3 (aromatic C), 78.9 (alkyne C), 75.5 (alkyne CH), 56.2 (CH₂), 41.8 (aliphatic C), 31.1 (CH₃) ppm. IR: $\tilde{\nu}$ = 3286, 3262, 3037, 2972, 2931, 2875, 2122, 1606, 1506, 1218, 1181, 1018 cm⁻¹. Elemental analysis for C₂₁H₂₀O₂: calcd. C 82.86, H 6.62%; found C 82.60, H 6.65%. This is a known compound [19].

2.4 Preparation of Composite Rocket Propellants

HMX was dried at 60 °C for a minimum of 72 h prior to use whereas prilled ADN was used as received. Standard mixing and vacuum casting techniques were applied in producing these propellants. When using NPBA-OMe, it was dissolved in the plasticizer overnight at 60 °C before mixing. The dialkyne curing agent BABE was dissolved in the plasticizer by heating the mixture prior to addition. The filler particles were dispersed in a submix consisting of GAP, plasticizer, NPBA, and other minor components and stirred at 55 °C. The mixture was casted under vacuum degassing and the casted propellant was cured at 60 °C for 120 h (dual curing or curing with N100) or 48 h (curing with BABE). When iso-

cyanates were utilized as curing agent, the isocyanate was added in the final step together with the curing catalyst (TPB), following the addition of all other constituents (including HMX).

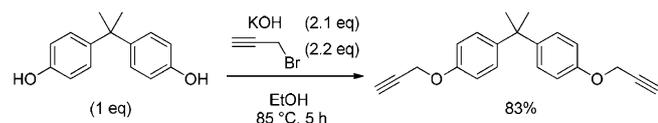
All components used in the propellant mixture were tested by DSC for possible compatibility issues with the new alkyne curing agent. In addition, vacuum thermal stability (VTS) testing was conducted for one of the propellant mixtures based on HMX cured with BABE at 100 °C for 40 h and was found that only 0.40 cm³ gas evolved per 5 g propellant. The compatibility issues of ADN and the energetic plasticizer TMETN were evaluated by us previously, and handling was found to be safe at mixing and curing temperatures (60 °C) [20].

3 Results and Discussion

3.1 Isocyanate-Free Curing of HMX-GAP-BuNENA Propellants

Due to the known and favorable mechanical properties of polyurethanes cured by the aromatic isocyanate MDI, we speculated whether a similar biaromatic moiety could be incorporated as part of a difunctional alkyne for isocyanate-free curing of azide prepolymers. Alkylation of a bisphenol with a propargyl halide with formation of a bisphenol bis(propargyl ether) would be an obvious choice, and the readily deprotonated phenolic functionalities of a bisphenol would serve as a suitable nucleophile. Due to the convenient availability of bisphenol A, we opted for preparation of bisphenol A bis(propargyl ether) (BABE). This is a known chemical compound, but we could not find most of the reported syntheses of it to be useful for preparation of substantial quantities of material (several hundred grams), mainly because of the use of impractical or hazardous solvents and/or reagents in these procedures.

We used the reported procedure by Liu et al. [19] as a foundation and applied a modified work-up as described in the Experimental Section in order to scale up the synthesis more effectively. A solution of potassium hydroxide and bisphenol A in ethanol was refluxed after addition of a solution of propargyl bromide in toluene (Scheme 2). The reaction product was isolated in high yield (83%) after filtration of the reaction mixture by addition of a carefully controlled quantity of water. The quantity of water was adjusted so that it would be sufficient to induce crystallization of the product from the filtered and alcoholic reaction mixture, but not so much as to cause phase separation of poorly water soluble toluene (commercial propargyl bromide is supplied as a solution in toluene). This gave a product of



Scheme 2. Synthesis of bisphenol A bis(propargyl ether) (BABE).

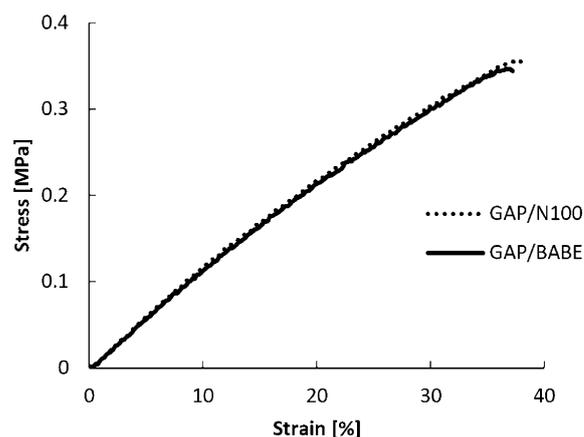


Figure 1. Tensile testing of GAP diol samples cured with either isocyanate (N100) or isocyanate-free curing agent (BABE) at 21 °C (crosshead speed = 50 mm min⁻¹).

fine quality directly, suitable for use without further purification.

Test samples of GAP diol prepolymer were cured with either a standard trifunctional isocyanate curing agent (N100), using an NCO/OH curing ratio of 1.0, or BABE alkyne curing agent, using a BABE/GAP ratio of 1.0 (all polymer samples were cured at 60 °C). The mechanical properties were evaluated from tensile testing of end-bonded samples at room temperature (Figure 1). As can be seen from Figure 1, stress-strain curves for GAP/N100 and GAP/BABE are virtually indistinguishable, both with regard to tensile strength, elastic modulus and elongation at break. Although merely a rough indication, curing of GAP with BABE may therefore prove useful for curing smokeless propellant formulations with GAP-based energetic binder systems.

In much detail, we have previously examined the mechanical properties of smokeless composite rocket propellants based on a GAP binder with HMX and/or ADN as energetic filler materials [18,20]. The propellant formulations we developed in that work had a solids loading of 60 wt-% and served as a starting point, on which we have introduced BABE as an isocyanate-free curing agent, allowing for expedient comparison. In addition, we wanted to incorporate a polymeric bonding agent (NPBA) in some of the samples to investigate whether they might be effective under isocyanate-free conditions and thereby deepen our understanding of the mode of function for this family of bonding agents [18].

Four propellant batches based on HMX filler (60 wt-%), GAP binder, and BuNENA plasticizer were mixed on a 500 g scale (Table 1, Figure 2). For benchmarking, one isocyanate-cured mixture with standard N100 curing agent (with NCO/OH = 1.0) and containing 0.05 wt-% NPBA-OMe was prepared. For comparison, three analogous propellant mixtures containing BABE alkyne curing agent were prepared. Two of these had a BABE/GAP curing ratio of 1.0, and one of them also contained 0.05 wt-% NPBA-OMe. The third

Table 1. HMX-GAP-BuNENA propellants cured with N100 or BABE.^{a)}

Constituent	HMX/N100/1.0/NPBA/wt-%	HMX/BABE/1.0/NPBA/wt-%	HMX/BABE/1.0/wt-%	HMX/BABE/1.3/wt-%
HMX (50–60 μm)	38.57	38.57	38.57	38.57
HMX (4–5 μm)	21.43	21.43	21.43	21.43
GAP diol	24.92	24.78	24.82	23.86
BuNENA	9.50	9.50	9.50	9.50
BABE	–	3.87	3.88	4.84
N100	3.70	–	–	–
TPB	0.03	–	–	–
NPBA-OMe	0.05	0.05	–	–
Stabilizers and minor components	1.80	1.80	1.80	1.80
NCO/OH	1.00	–	–	–
BABE/GAP	–	1.00	1.00	1.30
Pot life ($\tan \delta = 1$)/h	45.0	3.0	6.3	3.8
Mechanical properties (21 °C)^{b)}				
Max tensile strength/MPa	0.73	0.37	0.38	0.63
Strength at break/MPa	0.69	0.35	0.36	0.62
Elongation at σ_{max} /%	28.6	26.2	32.0	18.8
Elongation at break/%	30.2	33.3	33.5	19.1
Elastic modulus/MPa	4.1	3.1	2.4	6.0
Shore A hardness	58	49	48	65
Thermal properties				
T_g DMA 1 Hz/ $^{\circ}\text{C}^{\text{c}}$	–49.4	–42.2	–44.2	–37.1
DSC onset exotherm/ $^{\circ}\text{C}^{\text{d}}$	228.2	223.7	221.4	220.4
DSC initial onset exotherm/ $^{\circ}\text{C}^{\text{d}}$	170.2	172.9	173.6	170.9

a) All propellants were prepared on a 500 g scale. The formulations contain standard stabilizers for nitrate ester plasticizers. b) Crosshead speed = 50 mm min⁻¹. c) Determined by the loss modulus. d) Heating rate = 10 K min⁻¹.

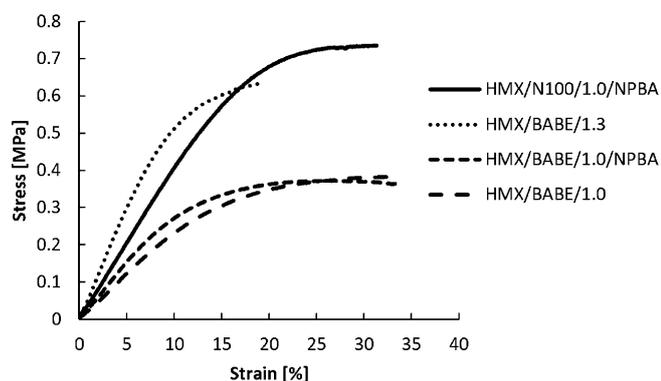


Figure 2. Tensile testing of HMX-GAP-BuNENA propellants at 21 °C (crosshead speed = 50 mm min⁻¹).

mixture was prepared with a BABE/GAP curing ratio of 1.3, but no NPBA-OMe was added. Tensile testing of propellant specimens from these four mixtures is presented in Figure 2.

The propellant mixture cured with BABE (BABE/GAP = 1.0, no NPBA-OMe) gave a tensile strength of 0.38 MPa, an elastic modulus of 2.4 MPa and an elongation at break of 33.5% (Table 1). Interestingly, we reported in our previous work that a comparable formulation, but using isocyanate N100 as the curing agent (NCO/OH = 1.0) has a similar tensile strength of 0.33 MPa and an elastic modulus of 2.5 MPa, but a somewhat better elongation (51.1%) at

break [18]. The propellant cured by BABE (BABE/GAP = 1.0) and containing NPBA-OMe had nearly identical mechanical characteristics to the mixture without NPBA-OMe (Figure 2), a preliminary indication that standard theory on the necessity of isocyanates for function of NPBAs is correct on this point [21–23]. We will briefly discuss the implications of this in the final section. Increasing the BABE/GAP curing ratio to 1.3 improved maximum tensile strength of the cured propellant to 0.63 MPa, but elongation at break was reduced to 19.1% (Table 1, Figure 2). Samples cured by BABE had a very satisfactory consistency and did not contain any bubbles or other discontinuities after completed curing; something that frequently is problematic when using the moisture sensitive and sometimes gas-forming isocyanates. In summary, curing of HMX-GAP-BuNENA smokeless formulations using BABE gave satisfactory mechanical characteristics, albeit with somewhat reduced elongation at break, compared to isocyanate cured propellants.

3.2 Dual Curing of HMX-GAP-BuNENA Propellants

Dual curing of hydroxyl-terminated azide prepolymers, denoting the combined use of an isocyanate and a non-isocyanate curing agent, is an alternative to the use of each curing system separately. It is attractive mainly because it allows for the simultaneous but mutually independent use of a difunctional isocyanate like IPDI (solely for chain exten-

Table 2. HMX-GAP-BuNENA Propellants cured with N100 or IPDI/BABE.^{a)}

Constituent	HMX/N100/1.0/NPBA/wt-%	HMX/Dual/wt-%	HMX/Dual/NPBA/wt-%
HMX (50–60 μm)	38.57	38.57	38.57
HMX (4–5 μm)	21.43	21.43	21.43
GAP Diol	24.92	24.40	24.34
BuNENA	9.50	9.50	9.50
BABE	–	1.97	1.98
N100	3.70	–	–
IPDI	–	2.28	2.28
TPB	0.03	0.05	0.05
NPBA-OMe	0.05	–	0.05
Stabilizers and minor components	1.80	1.80	1.80
NCO/OH	1.00	1.10	1.10
BABE/GAP	–	0.70	0.70
Pot life ($\tan \delta = 1$)/h	45.0	10.9	17.1
Mechanical properties (21 °C) ^{b)}			
Max tensile strength/MPa	0.73	0.51	0.82
Strength at break/MPa	0.69	0.48	0.78
Elongation at σ_{max} /%	28.6	31.8	20.0
Elongation at break/%	30.2	36.2	20.6
Elastic modulus/MPa	4.1	3.7	6.5
Shore A hardness	58	58	67
Thermal properties			
T_g DMA 1 Hz/°C ^{c)}	–49.4	–40.8	–40.1
DSC onset exotherm/°C ^{d)}	228.2	225.8	228.0
DSC initial onset exotherm/°C ^{d)}	170.2	168.7	173.6

a) All propellants were prepared on a 500 g scale. The formulations contain standard stabilizers for nitrate ester plasticizers. b) Crosshead speed = 50 mm min⁻¹. c) Determined by the loss modulus. d) Heating rate = 10 K min⁻¹.

sion) and a difunctional alkyne agent like BABE (for cross-linking) with formation of the crosslinked polymeric network. As such, chain extension and crosslinking can to some extent be adjusted independently when using the two systems jointly. Korean researchers have recently reported the beneficial mechanical characteristics that may result from such dual curing of hydroxyl-terminated GAP [12]. However, initial studies are not extended to complete propellant formulations.

We prepared two HMX-GAP-BuNENA propellant mixtures on a 500 g scale (Table 2), analogous to the ones detailed

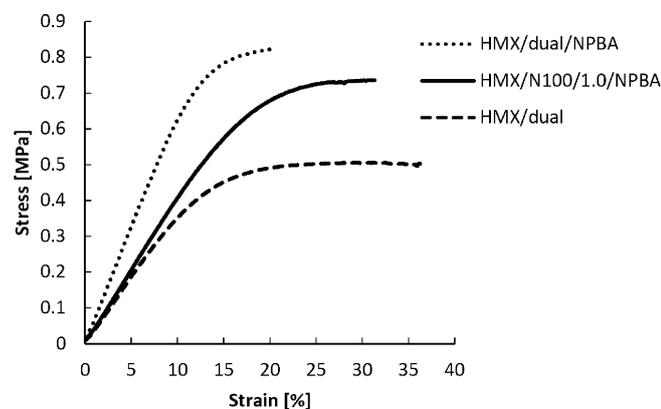


Figure 3. Tensile testing of dual cured HMX-GAP-BuNENA propellants at 21 °C (crosshead speed = 50 mm min⁻¹).

in the previous section, and used a dual curing system of IPDI (NCO/OH = 1.1) and BABE (BABE/GAP = 0.7) in both of them. The dual curing ratios were optimized by separate small scale experimentation on binder systems in advance. One of the two mixtures also contained 0.05 wt-% of NPBA-OMe. Tensile testing of cured propellant specimens is presented in Figure 3. The same “standard” mixture containing NPBA-OMe and cured with N100 isocyanate (used in Figure 2), is also included in Table 2 and Figure 3 for comparison. The propellant mixture cured with the dual curing system and containing NPBA-OMe gave the highest tensile strength of any of our HMX-GAP-BuNENA propellant mixtures so far (0.82 MPa), while still maintaining a moderate but useful elongation at break of 20.6% (Table 2). The identical propellant mixture without NPBA-OMe gave a significantly reduced tensile strength of 0.51 MPa, but an improved elongation at break of 36.2%. Again, we see the crucial function of isocyanates in order for the NPBA to take effect on binder-filler interactions, and the somewhat reduced elongation resulting from the use of NPBA, an effect we have clearly documented in previous work [18]. Overall, it appears that dual curing may be a useful and advantageous procedure to both utilize NPBA type bonding agents and give the most favorable strength/elongation ratios available in these nitramine-filled GAP propellant formulations.

Table 3. ADN/HMX-GAP-TMETN propellants cured with BABE or IPDI/BABE.^{a)}

Constituent	ADN/BABE/1.3/wt-%	ADN/HMX/BABE/1.3/wt-%	ADN/HMX/dual/NPBA/wt-%
Prilled ADN	60.00	45.00	45.00
HMX (50–60 μm)	–	10.00	10.00
HMX (4–5 μm)	–	5.00	5.00
GAP Diol	23.86	23.86	24.34
TMETN	9.50	9.50	9.50
BABE	4.84	4.84	1.98
IPDI	–	–	2.28
TPB	–	–	0.05
NPBA-OMe	–	–	0.05
Stabilizers and minor components	1.80	1.80	1.80
NCO/OH	–	–	1.10
BABE/GAP	1.30	1.30	0.70
Pot life (tan δ = 1)/h	4.7	3.8	10.2
Mechanical properties (21 °C) ^{b)}			
Max tensile strength/MPa	0.28	0.40	0.30
Strength at break/MPa	0.24	0.34	0.25
Elongation at σ _{max} /%	5.0	8.6	15.3
Elongation at break/%	9.3	12.6	22.0
Elastic modulus/MPa	7.8	7.1	3.1
Shore A hardness	46	42	53
Thermal properties			
T _g DMA 1 Hz/°C ^{c)}	–29.5	–29.0	–32.4
DSC onset exotherm/°C ^{d)}	171.9	172.3	162.1
DSC initial onset exotherm/°C ^{d)}	139.3	145.1	140.6

a) All propellants were prepared on a 500 g scale. The formulations contain standard stabilizers for nitrate ester plasticizers. b) Crosshead speed = 50 mm min⁻¹. c) Determined by the loss modulus. d) Heating rate = 10 K min⁻¹.

3.3 Isocyanate-Free and Dual Curing of ADN-Containing Propellants

We have recently published an extensive study on the mechanical properties of smokeless composite propellants containing prilled ADN [20], a high performance oxidizer with attractive ballistic properties, using GAP binder and TMETN plasticizer. We found that the mechanical properties of such isocyanate-cured ADN-GAP-TMETN propellants could be significantly improved by incorporation of HMX and NPBA, roughly doubling the tensile strength. Due to the well-documented compatibility issues between ADN and isocyanates [10,20], isocyanate-free curing systems are of particular interest for ADN propellants. Menke and co-workers have studied isocyanate-free curing of ADN propellants using BPS [8,9].

On a 500 g scale, we prepared three composite propellant formulations based on GAP diol binder and prilled ADN or ADN/HMX as energetic filler materials, all at a total of 60 wt-% solids loading as previously (Table 3). TMETN was chosen as plasticizer because ADN has poorer compatibility with BuNENA than with TMETN. The first mixtures contained prilled ADN as the only solid energetic material and were cured with BABE using a BABE/GAP ratio of 1.3. The second formulation only differed from the first in that one quarter of the prilled ADN was substituted by HMX of

two particle fractions. The third mixture was based on the second, but contained 0.05 wt-% NPBA-OMe and was subjected to IPDI/BABE dual curing (NCO/OH = 1.1, BABE/GAP = 0.7). We found that the BABE curing agent was less soluble in the GAP-TMETN binder system than in GAP-BuNENA, but the use of solvents was still not necessary. Prior to addition to the mixture, the dialkyne was dissolved in the TMETN-plasticizer upon heating to 73 °C (compared

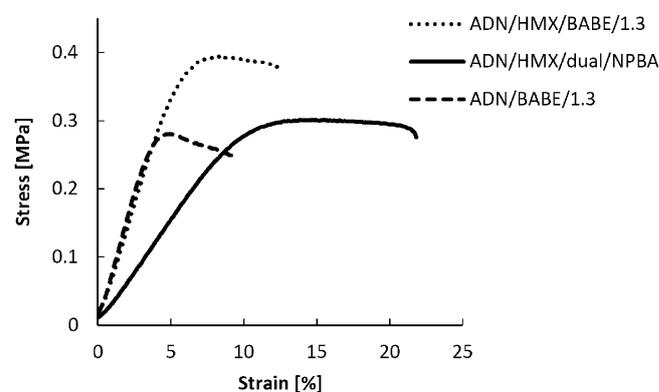


Figure 4. Tensile testing of ADN/HMX-GAP-TMETN propellants at 21 °C (crosshead speed = 50 mm min⁻¹).

to 60 °C for BABE in BuNENA), close to the melting point of BABE. This temperature was higher than the mixing temperature (60 °C) and thus it cannot be ruled out that some BABE may crystallize during processing and curing, thereby being partly or fully unable to contribute to the curing process.

Tensile test results of propellant specimens from the three ADN mixtures are presented in Figure 4. As we have noted earlier, propellants based on prilled ADN generally have distinctly poor mechanical characteristics, much due to the fact that ADN has an appreciable solubility in polar binder systems, affecting particle bonding [9]. The data presented in Figure 4 offer no exception. The propellants containing prilled ADN as the only energetic filler and cured by BABE have rather poor mechanical properties. Addition of HMX improved tensile strength considerably, but elongation at break is still only 12.6%. Of more interest is the third mixture, containing ADN-HMX and NPBA-OMe, which utilized the IPDI/BABE dual curing system. The cured propellant has similar tensile strength, but roughly doubled elongation at break. However, none of the propellants reported in Table 3 and Figure 4 have improved mechanical properties compared to those we have presented in our previous study [20], and we believe solubility issues of the isocyanate-free curing agent in the GAP-TMETN binder system could be a contributing factor to this observation. Continued optimization may perhaps improve mechanical properties. As data on mechanical characteristics of fully formulated ADN-containing propellants is sparse in open literature, there is currently limited material with which we can compare our results.

Conversely, one very important improvement of the ADN-containing propellants presented in this work is the fact that the dual curing system composed of IPDI and BABE successfully cured propellant with prilled ADN at 60 °C, using TPB as curing catalyst. In our previous work, these conditions almost exclusively provided unsuccessful "soft cure" of the propellant, even in the presence of special stabilizers, and we had to resort to room temperature curing using dibutyltin dilaurate (DBTDL) as curing catalyst [20]. Use of DBTDL is unwanted and frequently gives unacceptably short pot life of propellant mixtures. As such, although more work is needed to develop a solid alkyne curing agent with improved solubility in GAP-TMETN, dual curing systems may become an important method for preparation of smokeless compositions containing prilled ADN.

3.4 Thermal Characteristics of Isocyanate-Free and Dual Cured Smokeless Propellants

Compared to isocyanate curing agents, a known disadvantage of isocyanate-free curing systems is the resulting slight increase of the glass transition temperature (T_g) of the cured propellants [5–7]. We have measured T_g for all our composite propellants by dynamic mechanical analysis

(DMA) and the results are presented in Table 1, Table 2, and Table 3. In line with what has been presented by others, T_g is noticeably higher for propellants cured by BABE than those cured by isocyanates, and T_g is increasing with increasing quantities of BABE. The rather stiff biaromatic moiety of bisphenol A will almost certainly contribute to the elevated glass transition temperatures in a greater extent than aliphatic derivatives like BPS.

For propellants based on prilled ADN, GAP, and TMETN, T_g values are considerably higher than those for HMX, GAP, and BuNENA propellants. As described by Menke and co-workers, this is most probably due to the fact that ADN has a non-negligible solubility in TMETN plasticizer [9]. As we have shown previously, T_g can be efficiently lowered by including certain polyester or polyether polymers in the binder system [20]. However, addition of such non-energetic prepolymers is only possible under isocyanate or dual curing conditions as these substances do not contain azide functionalities.

In previous work, we have investigated low-temperature mechanical characteristics of isocyanate-cured HMX-GAP-BuNENA propellants and documented an increased elongation at break at lower temperatures when compared to room temperature [18]. For comparison, we also wanted to undertake tensile testing of propellants cured with BABE at lower temperatures. At NAMMO Raufoss, a 2.7 kg propellant batch was prepared, identical to the HMX/BABE/1.3 composition in Table 1. Tensile testing of propellant specimens was carried out at –30 °C.

As for isocyanate-cured propellants, an increased elongation at break was observed at lower temperatures. At room temperature, the identical propellant prepared at smaller scale had an elongation at break of 19.1% (Table 1), while at –30 °C, elongation at break increased to 29.4% (average of three propellant specimens, peak stress = 2.57 MPa). In analogy with the isocyanate-cured propellants [18], we believe semicrystalline behavior (strain-induced crystallization among them) for these energetic and polar binder systems at low temperature to be a decisive factor. However, the low temperature ductile behavior is much less pronounced for this propellant cured with BABE (BABE/GAP = 1.3) than for the isocyanate-cured mixtures investigated previously, where elongation at break may approach 100% at low temperatures. For a more extended discussion of such behavior, the reader should consult our previous publication [18].

Pot life (herein defined as when $\tan \delta = 1$ as measured by rheology) of our propellant compositions utilizing BABE curing agent is generally in the range of 3–6 h (Table 1, Table 2, and Table 3). As the curing reaction is a thermally activated Huisgen cycloaddition, pot life is very dependent on temperature, and pot life can be considerably extended at lower temperatures. However, as solubility of the alkyne curing agent in the binder system might be an issue, we kept the temperature at 60 °C both during processing and

curing to reduce the possibility of curing agent crystallization in the propellant.

3.5 Ballistic Properties of Isocyanate-Free Smokeless Propellants

Although we have focused our attention mainly on the mechanical characteristics of our smokeless propellant formulations, we have also evaluated their ballistic properties. We have performed calculations on the theoretical maximum specific impulse for HMX-GAP and ADN-GAP compositions [24]. The results from these calculations are presented in Figure 5. The ballistic performance of ADN with various other binder systems, including energetic polymer systems, can be found elsewhere [25].

From the 2.7 kg propellant batch prepared at NAMMO Raufoss, three 2" ballistic evaluation rocket motors were cast. Ballistic properties such as burning rate and pressure index were determined by static testing using three different nozzle sizes. The results are presented in Table 4. Ballistic properties are nearly identical to the very similar, but isocyanate-cured, propellant we have reported previously,

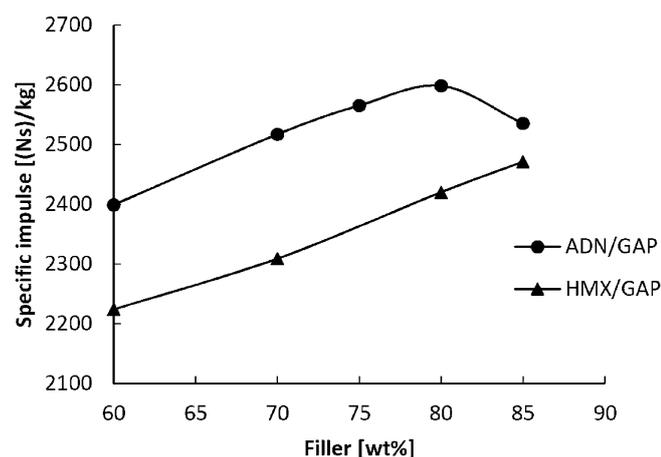


Figure 5. Theoretical maximum specific impulse of ADN-GAP and HMX-GAP propellants. Calculated with computer software at a chamber pressure = 6.9 MPa and nozzle-expansion ratio = 68.1:1 [24].

Table 4. Ballistic properties of isocyanate-free HMX-GAP-BuNENA composite propellant with 60% HMX solid loading at 21 °C.

Ballistic property	Value
Theoretical specific impulse ^{a)} I_{sp}	2163 Ns kg ⁻¹
Characteristic exhaust velocity ^{a)} c^*	1359 m s ⁻¹
Burning rate at 6.9 MPa ^{b)}	6.9 mm s ⁻¹
Burning rate at 10 MPa ^{b)}	8.9 mm s ⁻¹
Pressure exponent ^{b)}	0.68

a) Calculated with computer software at a chamber pressure = 6.9 MPa and nozzle-expansion ratio = 68.1:1 [24]. Data for bisphenol A was used as a substitute for BABE in these calculations. b) Determined by static testing of three 2" ballistic evaluation rocket motors in the pressure range 6–11 MPa.

although both burning rate and pressure exponent are slightly elevated [18]. The small increase of burning rate for isocyanate-free versus isocyanate-cured propellants has also been observed by Menke and co-workers [8,9].

As the propellant formulations presented in this work do not contain burning rate modifiers, the ballistic characteristics should only be regarded as a provisional starting point for further studies. At useful solid loadings, the specific impulse of these HMX-GAP-BuNENA smokeless propellants is fully comparable to or exceeding those of conventional extruded and cast double-base smokeless propellants [26].

3.6 Impact and Friction Sensitivity of Isocyanate-Free and Dual Cured Smokeless Propellants

We have tested the impact and friction sensitivities of some of our isocyanate-free and dual cured propellants for comparison to some of the analogous isocyanate cured smokeless propellants reported previously [20]. In addition, we have compared them to AP-HTPB propellants. Traditional AP-HTPB composite propellants prepared commercially by NAMMO Raufoss in general 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) when tested in the same apparatus as used for all our work [20].

We measured the impact sensitivity of the HMX-GAP-BuNENA propellant cured by BABE presented in Table 1 and Figure 2 (BABE/GAP = 1.0, no NPBA-OMe) to 4.5 Nm and the friction sensitivity to 216 N. The analogous propellant cured by the dual cure system and presented in Table 2 and Figure 3 (the sample with NPBA-OMe) had a measured impact sensitivity of 4.5 Nm and friction sensitivity of 192 N. In sum, these HMX-GAP-BuNENA compositions compare favorably with traditional AP-HTPB propellants.

We have previously shown that isocyanate-cured ADN propellants, otherwise analogous to the ADN or ADN-HMX propellants presented herein have impact sensitivities in the 2.5–3.5 Nm range when using ADN-HMX filler and ca. 6 Nm when using only prilled ADN as filler [20]. Friction sensitivities were measured to be in the 70–120 N range with ADN-HMX filler and 42 N when using only prilled ADN as filler [20]. Consequently, we found incorporation of HMX to increase the impact sensitivity and reduce the friction sensitivity. We have measured the impact sensitivity of the ADN-HMX propellant cured with BABE presented in Table 3 and Figure 4 (BABE/GAP = 1.3) to 2.5 Nm and friction sensitivity to 40 N. The impact sensitivity is therefore nearly identical to the isocyanate cured propellants, but the friction sensitivity is markedly increased, most probably due to the more rigid propellant obtained with the isocyanate-free curing system.

3.7 Mode of Function of Neutral Polymeric Bonding Agents (NPBAs)

We have for some time been particularly interested in the use of polymeric bonding agents (NPBAs) in smokeless propellant formulations based on GAP with energetic filler materials for improvement of the binder-filler interactions [18]. NPBAs are acrylic copolymers based mainly on acrylonitrile and first developed by Kim in the late 1980s [21–23]. According to conventional theory, the NPBA is adsorbed onto the surface of nitramine filler particles and free hydroxyl groups in the NPBA subsequently react with isocyanate to form tough and crosslinked polymer shells that combine covalently to the binder system, strengthening the propellant composite.

In previous work, we have unambiguously verified how these bonding agents improve binder-filler interactions in isocyanate cured systems through both tensile testing and DMA analysis of propellant composites [18]. We investigated and partly speculated on the exact mode of action for such polymeric bonding agents as we observed NPBAs to significantly increase viscosity of propellant mixtures during processing (before any curing could take place) already at very low concentrations. In addition, we found that NPBA containing a strongly reduced number of reactive hydroxyl groups, resulting from substitution of 2-hydroxyethyl acrylate with 2-methoxyethyl acrylate during preparation (NPBA-OMe), gave the same order of improvement in binder-filler interactions as “conventional” NPBA. However, NPBA-OMe will still contain reactive functionalities due to incorporation of chain transfer agent (2-mercaptoethanol) during polymerization and will react with isocyanates, but the degree of shell crosslinking is markedly reduced [18].

In order to ascertain the necessity of isocyanates in the proper function of NPBAs, we have included NPBA-OMe in several of the propellant formulations in this work (as detailed in previous sections), both in mixtures containing isocyanates and those without. We used NPBA-OMe in preference to other NPBAs because it has certain advantages during preparation and use, such as slightly improved solubility in the binder system. As already described, the NPBA-OMe only took noticeable effect in mixtures containing isocyanates. To further probe binder-filler interactions in more detail, we undertook DMA analyses of several of the propellant specimens. The results for some HMX-GAP-BuNENA propellants cured with BABE are presented in Figure 6 and those for HMX-GAP-BuNENA propellants cured with the IPDI/BABE dual curing system are presented in Figure 7. The damping factors ($\tan \delta$) are there plotted as a function of temperature for the different samples. As $\tan \delta$ is the ratio of the loss (viscous) modulus to the storage (elastic) modulus, a greater damping is an indication of reduced elastic response and increased dissipative energy losses due to viscous flow [18,27]. Decreased damping is consequently an indication of improved filler-binder interactions in the propellants.

In Figure 6, the two virtually similar propellant samples (BABE/GAP=1.0), differing only by the presence of NPBA-OMe, have nearly indistinguishable damping factors, another manifestation of the fact that NPBAs only take effect in the presence of isocyanates. The sample in Figure 6 containing no NPBA, but with a larger content of BABE shows a decreased damping, a reduction most probably correlated to the increased crosslinking density. A shift of the curve towards higher temperatures for this sample also indicates how T_g for the propellant sample is increased by the extended crosslinking. Figure 7 depicts damping factors for the two dual cured HMX-GAP-BuNENA propellants, one with NPBA-OMe and one without. In marked contrast to the samples cured with only BABE, the increased binder-filler interactions by the use of NPBA-OMe are evident here.

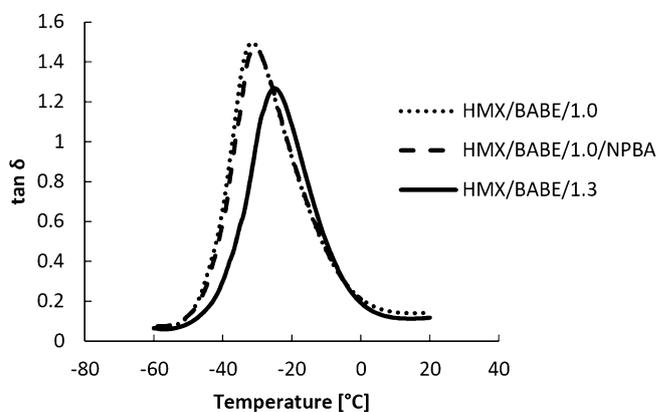


Figure 6. DMA analysis of isocyanate-free cured HMX-GAP-BuNENA propellants (oscillating frequency: 1 Hz, heating rate: 1 K min⁻¹, amplitude: 20 μ m).

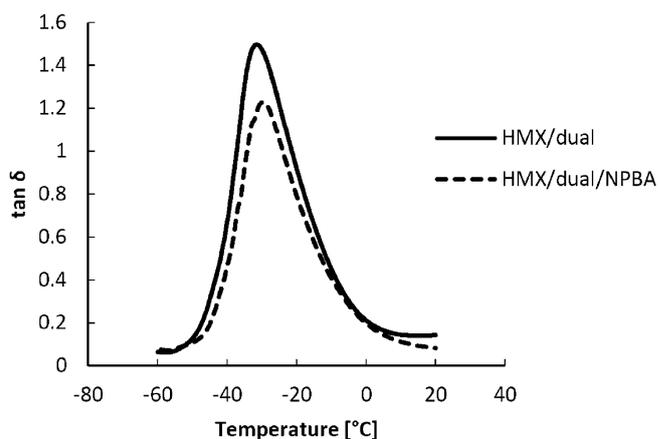


Figure 7. DMA analysis of dual cured HMX-GAP-BuNENA propellants (oscillating frequency: 1 Hz, heating rate: 1 K min⁻¹, amplitude: 20 μ m).

4 Conclusions

A new alkyne curing agent for azide-containing prepolymers, the crystalline bisphenol A bis(propargyl ether) (BABE), was efficiently synthesized on a large scale and used for isocyanate-free curing of several smokeless composite rocket propellant formulations based on GAP binder, BuNENA, or TMETN energetic plasticizers and HMX and/or ADN as energetic filler materials. Convenient and solvent-free processing and adequate to good mechanical characteristics, but somewhat increased glass transition temperatures, could be achieved by using BABE/GAP curing ratios of 1.0 or 1.3. Combining isocyanate (IPDI) and isocyanate-free (BABE) curing in the same system (dual curing) provided excellent mechanical properties to the propellant composites, especially if a neutral polymeric bonding agent (NPBA) was included.

The effect of NPBA on the binder-filler interactions was studied both under isocyanate and isocyanate-free curing conditions using tensile testing and DMA analysis. The presence of isocyanates was found essential in order for the NPBA to improve the binder-filler interactions. Accordingly, dual curing systems of IPDI and BABE, in addition to their adjustable and useful effect on mechanical characteristics, are compatible with the use of NPBA-type bonding agents. They can also be combined with polyether chain extenders for improvement of low temperature properties and seemed to improve curing quality in propellants based on prilled ADN (at 60 °C, using TPB curing catalyst) when compared to the use of isocyanate N100. As such, they are endowed with several qualities that may prove valuable in future developments.

Symbols and Abbreviations

ADD	Agency for Defense Development (Republic of Korea)
ADN	Ammonium dinitramide = $\text{NH}_4\text{N}(\text{NO}_2)_2$
AP	Ammonium perchlorate
BABE	Bisphenol A bis(propargyl ether)
BABE/GAP	Curing ratio, ratio of eq. BABE to eq. GAP diol
BHPB	1,4-Bis(1-hydroxypropargyl)benzene
BPS	Bispropargyl succinate
BuNENA	<i>N</i> -butyl-2-nitrateethylnitramine
DBTDL	Dibutyltin dilaurate
Desmodur N100	Hexamethylene diisocyanate biuret trimer
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
FOI	Swedish Defence Research Agency
GAP	Glycidyl azide polymer
HMX	Octogen, cyclotetramethylene tetranitramine
HTPB	Hydroxyl-terminated polybutadiene

IPDI	Isophorone diisocyanate
IR	Infrared
MDI	Methylene diphenyl diisocyanate
M_n	Number average molecular weight
M_w	Weight average molecular weight
NAMMO	Nordic Ammunition Group
NCO/OH	Curing ratio, ratio of isocyanate to hydroxyl functionalities
NMR	Nuclear magnetic resonance
NPBA	Neutral polymeric bonding agent
polyAMMO	Poly(3-azidomethyl-3-methyloxetane)
polyBAMO	Poly(3,3-bis(azidomethyl)oxetane)
RDX	Hexogen, cyclotrimethylene trinitramine
STANAG	Standardization Agreement (NATO)
$\tan \delta$	Tangent delta (tangent of the phase angle) or damping factor
T_g	Glass transition temperature
THF	Tetrahydrofuran
TMETN	Trimethylolethane trinitrate
TMPO	Trimethylolpropane oxetane, 3-ethyl-3-(hydroxymethyl)oxetane
TPB	Triphenyl bismuth
VTS	Vacuum thermal stability

Acknowledgments

We thank NAMMO Raufoss for conducting ballistic evaluation and testing impact and friction sensitivity of the composite propellants, as well as helpful collaboration during all parts of this work.

References

- [1] A. Provatas, *Energetic Polymers and Plasticizers for Explosive Formulation – A Review of Recent Advances*, DSTO-TR-0966, Commonwealth of Australia, Canberra, Australia **2000**.
- [2] A. P. Manzara, *Azido Polymers Having Improved Burn Rate*, U.S. Patent 5681904, **1997**, Minnesota Mining and Manufacturing Company, St. Paul, MN, USA.
- [3] R. Reed Jr., *Triazole Cross-Linked Polymers*, U.S. Patent 6103029, **2000**, The United States of America as represented by the Secretary of the Navy, Washington, DC, USA.
- [4] D. Ciaramitaro, *Triazole Crosslinked Polymers in Recyclable Energetic Compositions and Method of Preparing the Same*, U.S. Patent 6872266 **2005**, The United States of America as represented by the Secretary of the Navy, Washington, DC, USA.
- [5] T. Keicher, W. Kuglstatler, S. Eisele, T. Wetzel, H. Krause, Isocyanate-Free Curing of Glycidyl-Azide-Polymer (GAP) with Bis-Propargyl-Succinate, *39th Int. Annual Conference of ICT*, Karlsruhe, Germany, June 24–27, **2008**, p. 66/1–13.
- [6] T. Keicher, W. Kuglstatler, S. Eisele, T. Wetzel, H. Krause, Isocyanate-Free Curing of Glycidyl Azide Polymer (GAP) with Bis-Propargyl-Succinate (II), *Propellants Explos. Pyrotech.* **2009**, *34*, 210–217.
- [7] T. Keicher, W. Kuglstatler, S. Eisele, T. Wetzel, M. Kaiser, H. Krause, Isocyanate-Free Curing of Glycidyl-Azide-Polymer (GAP), *41st Int. Annual Conference of ICT*, Karlsruhe, Germany, June 29–July 2, **2010**, p. 12/1–15.

- [8] K. Menke, T. Heintz, W. Schweikert, T. Keicher, H. Krause, Approaches to ADN Propellants Based on two Different Binder Systems, *39th Int. Annual Conference of ICT*, Karlsruhe, Germany, June 24–27, **2008**, p. 15/1–14.
- [9] K. Menke, T. Heintz, W. Schweikert, T. Keicher, H. Krause, Formulations and Properties of ADN/GAP Propellants, *Propellants Explos. Pyrotech.* **2009**, *34*, 218–230.
- [10] H. Pontius, M. A. Bohn, J. Aniol, Stability and Compatibility of a New Curing Agent for Binders Applicable with ADN Evaluated by Heat Generation Rate Measurements, *39th Int. Annual Conference of ICT*, Karlsruhe, Germany, June 24–27, **2008**, p. 129/1–34.
- [11] M. Rahm, E. Malmström, C. Eldsäter, Design of an Ammonium Dinitramide Compatible Polymer Matrix, *J. Appl. Polym. Sci.* **2011**, *122*, 1–11.
- [12] B. S. Min, Y. C. Park, J. C. Yoo, A Study on the Triazole Cross-linked Polymeric Binder Based on Glycidyl Azide Polymer and Dipolarophile Curing Agents, *Propellants Explos. Pyrotech.* **2012**, *37*, 59–68.
- [13] R. Huisgen, 1,3-Dipolar Cycloadditions. Past and Future, *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 565–598.
- [14] H. C. Kolb, M. G. Finn, K. B. Sharpless, Click Chemistry: Diverse Chemical Function from a Few Good Reactions, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.
- [15] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective “Ligation” of Azides and Terminal Alkynes, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2599.
- [16] C. W. Tornøe, C. Christensen, M. Meldal, Peptidotriazoles on Solid Phase, [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides, *J. Org. Chem.* **2002**, *67*, 3057–3064.
- [17] W. Lwowski, *Azides and Nitrous Oxides*, in: *1,3-Dipolar Cycloaddition Chemistry* (Ed.: A. Padwa), Wiley-Interscience, New York, **1984**, Vol. 1, p. 559.
- [18] E. Landsem, T. L. Jensen, F. K. Hansen, E. Unneberg, T. E. Kristensen, Neutral Polymeric Bonding Agents (NPBA) and Their Use in Smokeless Propellant Formulations Based on HMX-GAP-BuNENA, *Propellants Explos. Pyrotech.* **2012**, *37*, 581–591.
- [19] F. Liu, W. Li, L. Wei, T. Zhao, Bismaleimide Modified Bis Propargyl Ether Bisphenol A Resin: Synthesis, Cure, and Thermal Properties, *J. Appl. Polym. Sci.* **2006**, *102*, 3610–3615.
- [20] E. Landsem, T. L. Jensen, F. K. Hansen, E. Unneberg, T. E. Kristensen, Mechanical Properties of Smokeless Composite Rocket Propellants Based on Prilled Ammonium Dinitramide, *Propellants Explos. Pyrotech.* published online, DOI: 10.1002/prop.201200004.
- [21] C. S. Kim, C. H. Youn, P. N. Noble, A. Gao, Development of Neutral Polymeric Bonding Agents for Propellants with Polar Composites Filled with Organic Nitramine Crystals, *Propellants Explos. Pyrotech.* **1992**, *17*, 38–42.
- [22] C. S. Kim, P. N. Noble, C. H. Youn, D. Tarrant, A. Gao, The Mechanism of Filler Reinforcement from Addition of Neutral Polymeric Bonding Agents to Energetic Polar Propellants, *Propellants Explos. Pyrotech.* **1992**, *17*, 51–58.
- [23] C. S. Kim, *Filler Reinforcement of Polyurethane Binder Using a Neutral Polymeric Bonding Agent*, U.S. Patent 4915755, Sacramento, California, USA **1990**.
- [24] S. Gordon, B. J. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications I. Analysis*, NASA Reference Publication 1311, **1994**, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH, USA.
- [25] A. H. Ghee, G. Santhosh, *Advances in Energetic Dinitramides: An Emerging Class of Inorganic Oxidizers*, World Scientific Publishing Co., Singapore, **2007**, p. 139.
- [26] N. Wingborg, S. Andreasson, J. de Flon, M. Johnsson, M. Liljedahl, C. Oscarsson, Å. Pettersson, M. Wanhatalo, Development of ADN-based Minimum Smoke Propellants, *46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, Nashville, TN, USA, July 25–28, **2010**.
- [27] J. M. Kennedy, D. D. Edie, A. Banerjee, R. J. Cano, Characterization of Interfacial Bond Strength by Dynamic Analysis, *J. Compos. Mater.* **1992**, *26*, 869–882.

Received: July 16, 2012

Revised: September 18, 2012

Published online: November 27, 2012