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Curing of Glycidyl Azide Polymer (GAP) Diol Using Isocyanate, Isocyanate-Free, Synchronous Dual, and Sequential Dual Curing Systems

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Abstract: Glycidyl azide polymer (GAP) is an important energetic binder candidate for new minimum signature solid composite rocket propellants, but the mechanical properties of such GAP propellants are often limited. The mechanical characteristics of composite rocket propellants are mainly determined by the nature of the binder system and the binder-filler interactions. In this work, we report a detailed investigation into curing systems for GAP diol with the objective of attaining the best possible mechanical characteristics as evaluated by uniaxial tensile testing of non-plasticized polymer specimens. We started out by investigating isocyanate and isocyanate-free curing systems, the latter by using the crystalline and easily soluble alkyne curing agent bispropargylhydroquinone (BPHQ). In the course of the presented study, we then assessed the feasibility of dual curing systems, either by using BPHQ and isophorone diisocyanate (IPDI) simultaneously (synchronous dual curing), or by applying propargyl alcohol and IPDI consecutively (sequential dual curing). The latter method, which employs propargyl alcohol as a readily available and adjustable hydroxyl-telechelic branching agent for GAP through thermal triazole formation, gave rise to polymer specimens with mechanical characteristics that compared favorably with the best polymer specimens obtained from GAP diol and mixed isocyanate curatives. The glass transition temperature (T_g) of non-plasticized samples was heightened when triazole-based curing agents were included, but when plasticized with nitratoethylnitramine (NENA) plasticizer, T_g values were very similar, irrespective of the curing method.

Keywords: GAP · Branched GAP · Isocyanate curing · Azide-alkyne curing · Dual curing

1 Introduction

In solid propellant rocketry, propulsion units in fielded and currently operational missile systems are founded upon a relatively small number of firmly established propellant technologies, most of which have an extensive historical track record. While propulsion systems with either limited or no restrictions with respect to exhaust plume signature have their basis in ammonium perchlorate (AP) composites with inert binder systems (preferably aluminized), smokeless systems are based on nitrate ester plasticized binders (nitrocellulose, polyethers, polyesters) with or without nitramine filler materials [1]. Combination of the two sorts gives rise to the high-performance propellant types important in domains such as submarine-launched ballistic missiles, applications where performance with regards to specific impulse is particularly critical [2].

Although implemented propellant technology has now remained somewhat static for a considerable period of time, new incentives have accelerated the development of new generations of solid rocket propellants. Increasingly stringent legislature associated with the handling and use of many chemical species traditionally used in rocket propellant formulations (heavy metal compounds, perchlorates, isocyanates), when assessed in conjuncture with a tightening export bureaucracy and the diminishing production base for many important raw materials (a result of plant closures and industry consolidation during recent decades), have all contributed to an increased willingness by relevant manufacturers to evaluate new propellant candidates.

The bulk of contemporary research efforts directed towards new solid rocket propellant candidates is concentrated around new energetic binder systems and chlorine-free filler materials, as well as associated formulation additives (curing agents, bonding agents, burning rate modifiers) [3–

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19]. Research in the context of new smokeless propellants is particularly vibrant due to the poor sensitivity characteristics of traditional XLDB propellants (which have dual content of nitramine fillers and sensitive nitrate ester plasticizers).

Among new energetic binders, which in this context refer to binders that have not yet been implemented in propulsion systems, glycidyl azide polymer (GAP) is perhaps the most important and widely applied among them, having a history going back to the 1970s [20]. This partly stems from its commercial availability, energetic performance, moderate sensitivity, and high chemical stability. In addition, the content of azide functionalities in GAP opens up for isocyanate-free curing systems.

In spite of nearly continuous developmental work taking place since the 1970s, certain aspects of the application of GAP binders, specifically those concerning mechanical characteristics, remain problematic. Research focused on GAP binder systems and associated fillers is currently in rapid progress, especially since about 2008 [4–8,10–18]. Particularly, the use of polyfunctional alkynes for isocyanate-free curing of GAP under triazole formation is prevalent [4–8,10,13,14,16–18]. At the same time, the curing of azide- or alkyne-telechelic polyether/ester prepolymers in a more general context, using corresponding azide or alkyne curatives, is expanding, although such binder systems have little inherent energetic performance when not plasticized [21].

At FFI and NAMMO, we have recently reported some results from our developmental work pertaining to smokeless composite rocket propellants based on plasticized GAP binder containing nitramine and/or dinitramide filler materials [11–13]. In the presented work, we report on our detailed investigations into the mechanical characteristics of cured GAP diol binder systems, focusing on the GAP binder system. We examine isocyanate, isocyanate-free and dual curing systems, and make a comparison of the typical characteristics of each system. As part of our studies, we explore the attractive possibility of employing propargyl alcohol as a facile and tunable hydroxyl-telechelic branching agent for preparation of branched GAP polyols, a procedure we have named sequential dual curing.

2 Experimental Section

2.1 Chemicals

GAP diol (two batches with $M_n = 1904$, $M_w = 2075$, equivalent weight = 1220 and $M_n = 1796$, $M_w = 1951$, equivalent weight = 1230) was acquired from Eurenco (France), hexamethylene diisocyanate biuret trimer (Desmodur N100) from Bayer MaterialScience, 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-nitratoethylnitramine (BuNENA) was acquired from Chemring Nobel AS (Norway). All other chemicals were received from conventional laboratory suppliers such as Sigma-Aldrich and VWR, and were used without further purification.

2.2 Instruments and Analysis

Uniaxial tensile testing was conducted with an 810 MTS (Material Testing System), using microtensile specimens prepared according to ASTM D1708. For testing, a pair of customized aluminum tensile grips were designed and manufactured at FFI (Figure 1). Pieces forming the tensile grips were cut from aluminum using a water jet cutter. All tensile testing was conducted at room temperature, using a crosshead speed of 50 mm min^{-1}.

Dynamic mechanical analysis (DMA) was performed with a DMA 2980 from TA Instruments (dual cantilever clamp, specimen size: 40×10×4 mm). Differential scanning calorimetry (DSC) was carried out with a DSC Q1000 from TA Instruments. Rheology properties (oscillatory, 1 Hz) were measured with an Anton Paar Physica UDS 200 rheometer with an MP30 spindle (25 mm, 0° cone). Infrared (IR) spectroscopy was performed with a Nicolet iS10 spectrometer equipped with a DTGS KBR detector and a diamond HATR crystal. ^{1}H NMR and ^{13}C NMR spectra were recorded with

Figure 1. Tensile testing of dog bone-shaped, non-plasticized polymer samples (microtensile specimens according to ASTM D1708) using customized aluminium tensile grips. The picture is taken in the midst of an actual tensile test.

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a Bruker AVII 400 spectrometer operating at 400 MHz (^{1}H) and 100 MHz (^{13}C). Chemical shifts are reported in parts per million (δ) relative to internal reference of the solvent: 7.24/77.0 for $CDCl_3$. Elementary analysis was carried out by Eurofins MikroKemi AB in Uppsala, Sweden.

2.3 Preparation of Polymer Specimens

Polymer samples were prepared by manual mixing, using a glass rod, of the relevant constituents (prepolymer, curing agents, curing catalyst) in aluminum molds until the mixtures became homogeneous. The mixtures were degassed under vacuum (5–20 mbar) for 10–15 min at 60 °C and transferred to PTFE molds (109×45 mm) that had been lined with aluminum foil. The samples were degassed a second time and cured at 60 °C. All samples cured with isocyanates contained 0.05 % TPB as curing catalyst. Appropriate curing times were determined by monitoring the rheological properties.

Cautionary Note: Formation of triazoles by curing of GAP with alkynes is exothermic, and we urge all researchers to exercise caution. Excessively high curing ratios and/or large batch sizes may possibly give rise to dangerous temperature excursions, especially under essentially adiabatic conditions.

2.4 Synthesis of Bispropargylhydroquinone (BPHQ)

Modifying a preparatory procedure from the patent literature [22], bispropargylhydroquinone was prepared by a Williamson ether synthesis in the following manner: A 500 mL round-bottomed flask equipped with a large oval stirring bar (50×20 mm) was charged with acetone (300 mL) and propargyl bromide solution (80 wt-% in toluene, 89.4 g, 601 mmol). Hydroquinone (30.1 g, 273 mmol) was added and dissolved upon stirring, giving a clear solution. Under vigorous stirring, potassium iodide (4.54 g, 27.3 mmol, 10 mol-%) was added, followed shortly by portion wise addition of powdered anhydrous potassium carbonate (83.0 g, 601 mmol) via a powder funnel. The reaction flask was equipped with only a *loose* glass stopper to exclude free air admittance (but no reflux condenser), placed in a fluoropolymer-coated aluminum heating mantle that was heated to 60 °C (mantle temperature) and stirred in this condition overnight (ca. 19 h). As there is a temperature gradient associated with the use of the heating mantle, the reaction mixture was close to, but not boiling (only a negligible evaporative loss of acetone overnight). Activated charcoal (ca. four teaspoons) was added and stirring was continued for 5 min. The reaction mixture was filtered using a large folded paper filter (330 mm). The reaction flask and filter cake were washed with acetone (4×100 mL), and the combined organic phase was evaporated under vacuum to give a brown solid. The solid was dissolved upon gentle heating after addition of ethanol (95 vol-%, 300 mL). The clear, brown solution was poured into a 500 mL beaker and allowed to cool to room temperature. Crystallization was induced by addition of a few seed crystals, and water (100 mL) was added in small portions whilst stirring to aid further crystallization. After the addition, the beaker was left at 3 °C for 3 h to complete the crystallization process. The crystals were isolated by vacuum-filtration and dried at room temperature to give bispropargylhydroquinone (39.2 g, 77 % yield) as small, beige, and fluffy crystals of excellent purity. M.p. 47–49 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.91$ (s, 4 H, aromatic H), 4.62 (d, $J = 2.4$ Hz, 4 H, CH_2), 2.49 (t, $J = 2.4$ Hz, 2 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.4$ (aromatic C), 116.0 (aromatic C), 78.8 (alkyne C), 75.4 (alkyne C), 56.5 (CH_2) ppm. IR: $\tilde{\nu} = 3272$, 2915, 2863, 2130, 1504 cm^{-1}. $C_{12}H_{10}O_2$: calcd. C 77.40, H 5.41 %; found C 77.65, H 5.35 %. Compatibility tests with GAP and BuNENA were conducted by DSC experiments according to the guidelines of STANAG 4147.

3 Results and Discussion

3.1 Curing of GAP Diol with Isocyanate Curing Systems

By far the most important curing method for GAP diol/triol propellant binders is treatment with aromatic or aliphatic polyfunctional isocyanates, preferably the non-volatile aliphatic ones because of their lower toxicity and decreased reactivity, allowing for adequate pot-life and concomitant propellant processing. We have recently reported work pertaining to the mechanical characteristics of isocyanate-cured and plasticized GAP-nitramine propellant compositions [11–13], including compositions containing prilled ammonium dinitramide (ADN) [12,13]. In Scheme 1, the various curing mechanisms, curing systems and curing agents for GAP diol that are discussed in this work are summarized.

In order to more fully investigate the influence of the polymerization and crosslinking processes taking place during cure and understand how they relate to the mechanical characteristics of the completed propellant composite, we wanted to isolate the influence of the curing system by conducting a series of uniaxial tensile tests of unfilled and non-plasticized polymer specimens. In order to do so in a satisfactory manner, we developed a set of customized tensile grips designed specifically for soft, elastomeric polymer samples. We found the standardized experimental set-up for tensile testing of propellant composites unsuited for unfilled polymer samples because of their soft character and extensive elongation prior to break, causing the end pieces of the dog bone samples to partially glide and flow into the constricted section of the sample holder, thereby confounding the test results.

As a result, we prepared a set of customized aluminum tensile grips, where the end pieces of microtensile specimens are clamped, and the grip on the end pieces is tightened as the sample is elongated by the self-correcting tensile grip contact pieces (Figure 1), this being very similar to

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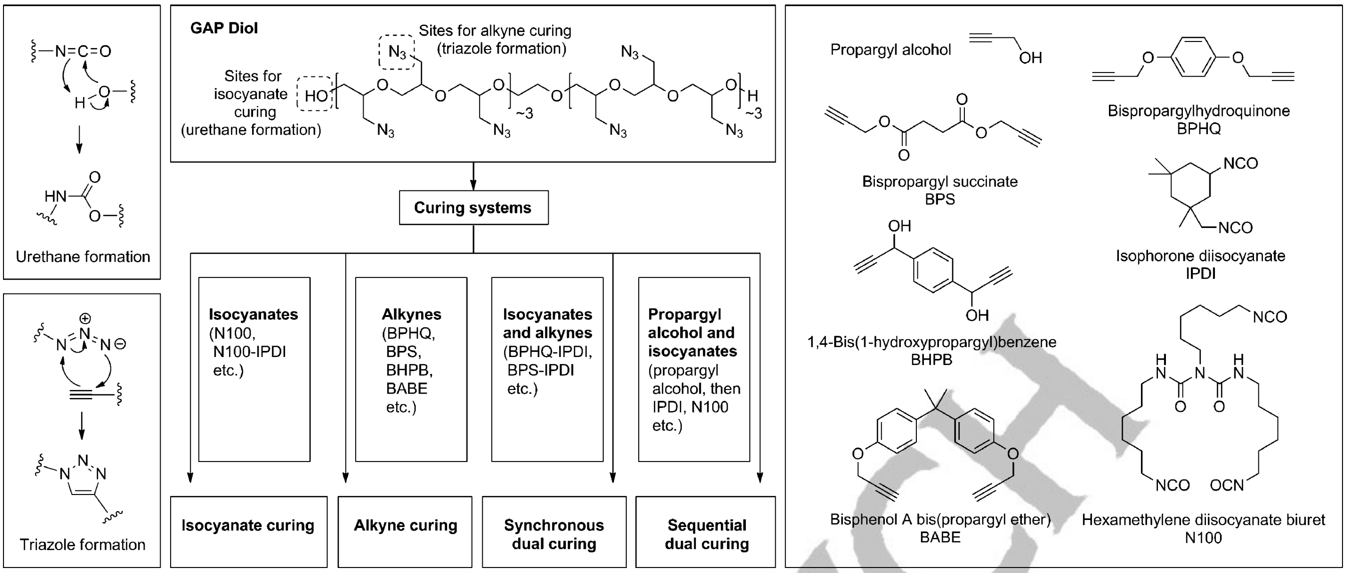

Scheme 1. Overview of curing mechanisms, curing systems, and curing agents for GAP diol.

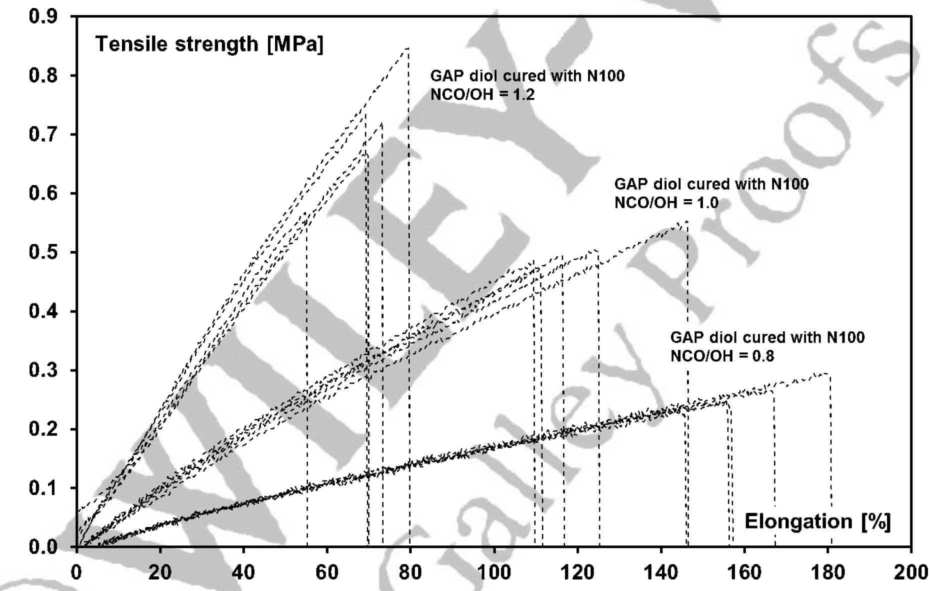

Figure 2. Tensile testing of polymer samples prepared from GAP diol and isocyanate N100 at varying curing ratios. Five parallels were tested for each curing ratio (tabulated data in Table 1).

conventional equipment used for tensile testing of such specimens. Screw-fastened contact pieces, on the other hand, are unsuited because of the sample thinning taking place during elongation. We found tensile testing using the customized tensile grips to have an excellent degree of reproducibility.

In Figure 2 (tabulated data for Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6 in Table 1), stress-strain curves for three test series (each containing five parallels) of GAP diol samples cured with isocyanate N100 at varying curing ratios (the NCO/OH molar ratio) are depicted. This test series functioned as a sort of reference system for further evaluations, and as anticipated, the strength is increased and the elongation is correspondingly reduced by increasing the curing ratio.

It is customary in solid rocket propellant manufacturing to combine isocyanate N100 with isophorone diisocyanate (IPDI) in order to adjust chain extending and crosslinking reactions taking place during the curing process, striking the best possible balance between propellant strength and elongation. In Figure 3, stress-strain curves for three test series of GAP diol samples cured with mixed isocyanates at

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Table 1. Mechanical characteristics of polymer samples prepared from GAP diol and various curing systems.

Curing system[a]	Tensile strength[b] [MPa]	Elongation at break[b] [%]	Elastic modulus[b] [MPa]
N100 (0.8)	0.26 (0.02)	161 (13)	0.180 (0.002)
N100 (1.0)	0.50 (0.03)	122 (15)	0.47 (0.03)
N100 (1.2)	0.7 (0.1)	69 (9)	1.09 (0.07)
N100-IPDI (1.0)	0.23 (0.03)	285 (23)	0.082 (0.004)
N100-IPDI (1.2)	0.52 (0.02)[c]	192 (7) [c]	0.315 (0.008)[c]
N100-IPDI (1.4)	0.76 (0.06)	147 (11)	0.60 (0.01)
BPHQ (1.0)	0.34 (0.02)	68 (4)	0.55 (0.02)
BPHQ (1.3)	0.57 (0.03)	48 (2)	1.24 (0.07)
BPHQ-IPDI (0.5/1.0)	0.60 (0.05)	95 (11)	0.71 (0.04)
BPHQ-IPDI (0.7/1.0)	0.85 (0.04)	72 (3)	1.28 (0.03)
Prop.alc.-IPDI (0.5/1.0)	0.79 (0.09)	157 (18)	0.57 (0.01)
Prop.alc.-IPDI (0.7/1.0)	1.2 (0.1)	117 (13)	1.11 (0.04)

a) The number in parenthesis following the curing system designation refers to the relevant curing ratio (see corresponding Figure). b) Mean value of five parallels (unless otherwise noted) with standard deviation values in parenthesis. c) Mean value of four parallels.

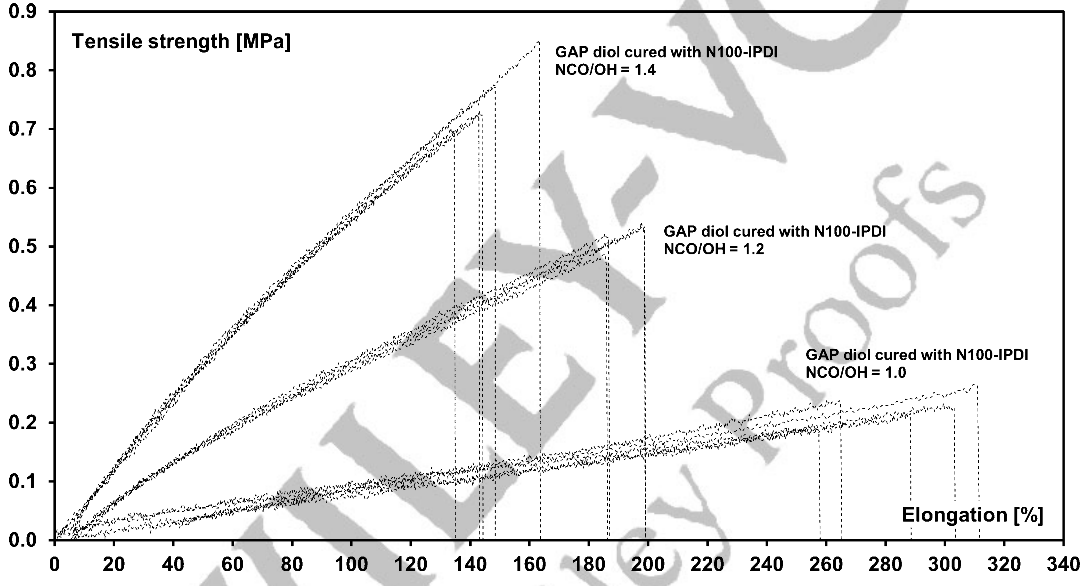

Figure 3. Tensile testing of polymer samples prepared from GAP diol and N100-IPDI isocyanate mixture (1:1 with respect to isocyanate content) at varying curing ratios. Four or five parallels were tested for each curing ratio (tabulated data in Table 1).

a constant N100/IPDI ratio and varying curing ratios are depicted. The N100/IPDI ratio was kept at a 1:1 ratio with respect to the isocyanate content of the respective curing agents. With an isocyanate content of 195 g of N100 per mol NCO for N100 and 112 g of IPDI per mol NCO for IPDI, this corresponds to an approximate N100/IPDI mass ratio of 1.74.

By comparison of Figure 2 and Figure 3, it is apparent that by employing N100-IPDI mixtures, considerably improved stress-strain behavior and corresponding sample toughness can be obtained relative to the use of N100 independently. Using N100 and a curing ratio of 1.2, a maximum tensile strength in the region of 0.7 to 0.8 MPa was obtained at an elongation of ca. 75% at break, while use of the N100-IPDI mixture and a curing ratio of 1.4 gave a similar maximum tensile strength of 0.7 to 0.8 MPa, but at a rough doubling of the elongation at break to approximately 150%.

3.2 Isocyanate-Free Curing of GAP Diol with Bispropargylhydroquinone (BPHQ)

The use of polyfunctional alkynes as alternative, isocyanate-free curing agents for GAP binder systems is by now well-established, at least at the laboratory scale [4–8,10,13,14,16–18]. Although a variety of such agents have been developed, the most comprehensibly explored ones have been bispropargyl succinate (BPS) [4–8,14,18], particularly by researchers from the Fraunhofer ICT in Germany, and 1,4-bis(1-hydroxypropargyl)benzene (BHPB) by researchers from the Agency for Defense Development (ADD) in the Republic of Korea [10]. Lately, other alkyne curing

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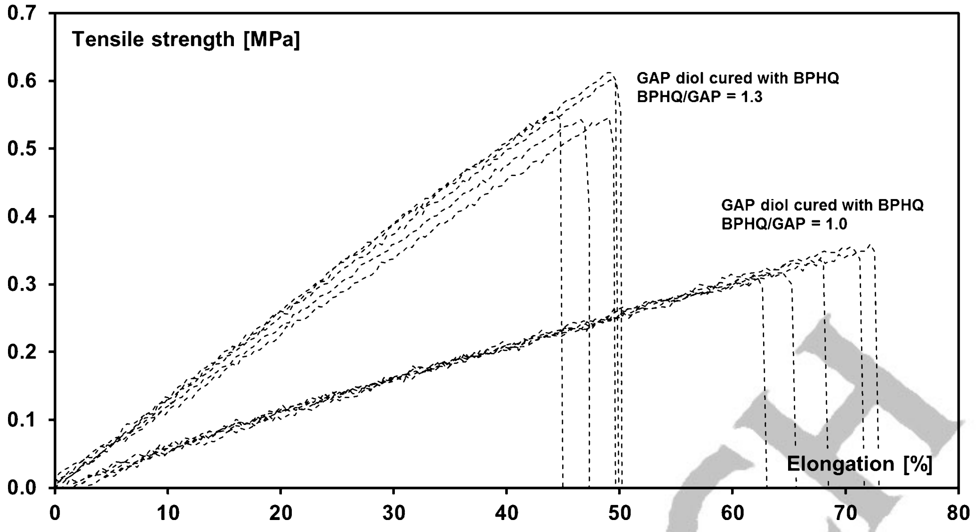

Figure 4. Tensile testing of polymer samples prepared from GAP diol and BPHQ at varying BPHQ/GAP molar ratios. Five paralells were tested for each curing ratio (tabulated data in Table 1).

agents such as 2,2-bis(prop-2-ynyl)malonate (DDPM) have been investigated by Chinese researchers [17]. We recently introduced bisphenol A bis(propargyl ether) (BABE) as an alkyne curing agent for GAP binder systems [13].

A useful alkyne curing agent for GAP binders must fulfil a number of criteria in order to allow propellant processing at larger scales. Besides providing sufficient pot-life for processing and imparting adequate mechanical qualities in the finished propellant composite, the curing agent must also be applicable for large scale synthesis and have a favorable solubility/miscibility with the GAP binder system so that its application is not associated with troublesome or resource-demanding procedures. As such, a facile preparation of a crystalline curing agent from inexpensive and amenable precursors, using purification by recrystallization, is probably preferable to production processes including dangerous reagents and/or unit operations such as vacuum distillation (distillation of propargyl compounds can be hazardous) or column chromatography, issues routinely encountered in the preparation of the curing agents BPS, BHPB, and DDPM [6,10,17,21d]. Such issues were partially the reason for our introduction of the BABE curing agent [13]. However, it is endowed with a rather moderate solubility in GAP diol, thereby habitually necessitating heat treatment of the binder for complete dissolution, something which can be problematic as the curing reaction (triazole formation by cycloaddition) is highly temperature-dependant. In addition, it can occasionally give rise to partial precipitation during cure if the system is allowed to cool prematurely, depending on the presence of plasticizer(s).

For the presented study, using non-plasticized GAP diol binder, a more convenient alkyne curing agent was needed, and none of the existing ones fulfilled our requirements. We therefore opted for introduction of the difunctional propargyl ether of hydroquinone for this purpose, a compound referred to herein as bispropargylhydroquinone (BPHQ) in order to follow the conventional nomenclature of alkyne curing agents in solid propellant rocketry. Like BABE, BPHQ is a crystalline material amenable to facile recrystallization, but unlike BABE, it is more soluble in GAP (also reflected in its lower melting point of ca. 50 °C). Although numerous syntheses of BPHQ are known from literature, we found nearly all of them unsuited at larger scales. The reason for this is that the electron-rich hydroquinone, if deprotonated quantitatively and primed for a Williamson ether synthesis, oxidizes/polymerizes in minutes, giving rise to tarry reaction mixtures. Reported procedures are therefore rarely useful for preparation of anything more than analytical quantities of material. However, using a procedure from the patent literature as a starting point [22], we introduced a number of modifications, including removal of a laborious extraction process and introduction of a simple recrystallization procedure in aqueous ethanol, to afford high-quality BPHQ in requisite quantities.

BPHQ is a convenient alkyne curing agent for GAP, and in Figure 4, stress-strain curves for two test series of GAP diol samples cured with BPHQ at two different BPHQ/GAP molar ratios are depicted. Compared with the isocyanate-cured samples tested in the same equipment (Figure 2 and Figure 3), the mechanical characteristics are rather poor (elongations at break lower than 100%, with tensile strengths in the region of only 0.3 to 0.6 MPa), especially in comparison with the samples cured with mixed isocyanates (Figure 3). The superiority of isocyanate vs. alkyne curing systems is well-known [10], and it is probably connected to the fact that alkyne curing agents couple randomly along GAP polymer chains and do not exploit the entire chain length to the same extent as a curing agent targeting the telechelic functionalities selectively. On the positive side though, alkyne curing systems, unlike isocyanates, are total-

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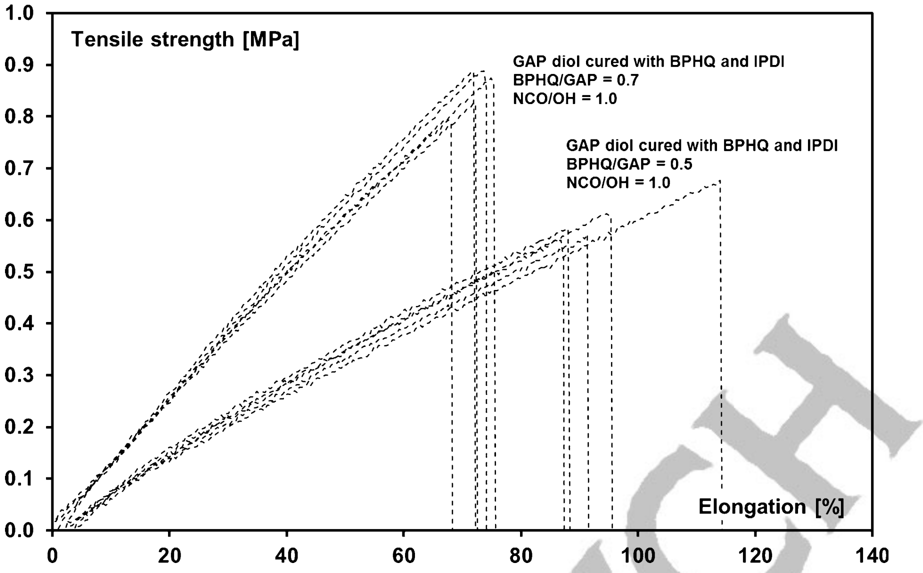

Figure 5. Tensile testing of polymer samples prepared from GAP diol and the BPHQ-IPDI synchronous dual curing system at varying BPHQ/GAP molar ratios. The NCO/OH curing ratio was 1.0 for both series, and there were five parallels for each BPHQ/GAP ratio (tabulated data in Table 1).

ly unaffected by moisture and gave rise to excellent, completely void-free polymer textures.

3.3 Synchronous Dual Curing of GAP Diol with BPHQ and IPDI

While the pre-eminence of isocyanates relative to alkynes with respect to the mechanical properties of cured GAP samples is fairly well established, the combination of the two curing modes, a method referred to as dual curing, can give rise to excellent mechanical characteristics [10,13]. It is particularly attractive since chain extension and crosslinking processes can thereby be adjusted quite independently of each other by using IPDI for the former and the alkyne for the latter. In order to distinguish this type of dual curing, where isocyanates and alkynes are used in a simultaneous fashion, from the procedure we introduce in the next section, we have named this traditional form of dual curing for synchronous dual curing.

Stress-strain curves for two test series of GAP diol samples cured using a combination of BPHQ and IPDI at two different BPHQ/GAP molar ratios are summarized in Figure 5. The NCO/OH curing ratio was kept at 1.0 for both series, and the BPHQ/GAP ratios were fixed at 0.5 and 0.7, respectively. Comparing Figure 5 with Figure 2, Figure 3, and Figure 4, the BPHQ-IPDI dual curing system performs much better than BPHQ separately, more than doubling the tensile strength at comparable elongations. The performance of this particular dual curing system is comparable to isocyanate curing using N100 (Figure 2), but it falls short of the favorable mechanical characteristics obtained from the use of the N100-IPDI mixture (Figure 3).

3.4 Branched GAP – Sequential Dual Curing of GAP Diol with Propargyl Alcohol and IPDI

It has been reported that under dual curing conditions, an aliphatic alkyne curing agent such as BPS is preferable to an aromatic alkyne curing agent such as BHPB, although the difference may be small under isocyanate-free conditions [10]. The development of an aliphatic alkyne curing agent for dual curing systems therefore felt obvious. However, we reasoned that given the difficulty of obtaining better mechanical characteristics than those obtained by using an optimized mixture of N100-IPDI isocyanates, and the need for employing custom synthesis in order to access new difunctional alkyne curing agents, we decided to explore whether commercially available and affordable monofunctional alkynes would suffice. As it is customary in polymer science to opt for a higher degree of telechelic functionalities in a polymer to heighten the degree of crosslinking and adjust the mechanical properties during the curing process, for example by employing GAP triol instead of GAP diol, we contemplated whether it would in fact be possible to obtain hydroxyl-telechelic, branched GAP of nearly any desired functionality by branching GAP diol with propargyl alcohol.

The preparation of branched, hydroxyl-telechelic GAP by combined degradation (chain cleavage) and azidation of high molecular weight polyepichlorohydrin has been studied extensively by Ahad and co-workers in Canada during the late 1980s and early 1990s [23]. Instead of using such customized GAP, linear GAP diol can be branched to virtually any desired degree of functionalization with propargyl alcohol through azide-alkyne thermal cycloaddition [24]. Interestingly, such propargyl alcohol branched GAP seems

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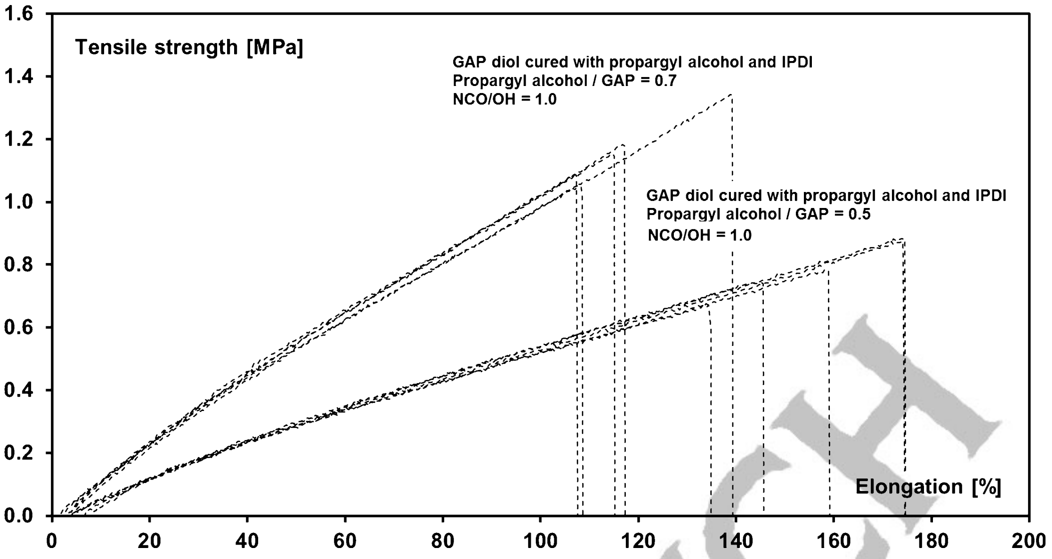

Figure 6. Tensile testing of polymer samples prepared from propargyl alcohol branched GAP diol and IPDI (sequential dual curing) at varying propargyl alcohol/GAP molar ratios. The NCO/OH curing ratio was 1.0 for both series, and there were five parallels for each propargyl alcohol/GAP ratio (tabulated data in Table 1).

only to have been investigated as a means of tailoring the burning rate behavior and not as a tool for improving the mechanical characteristics of cured GAP. Other branched GAP-triazoles have also been reported very recently, but hydroxyl-functional ones were apparently not included [25].

Because of the volatility of propargyl alcohol and the need to degas polymer samples under vacuum as part of the casting procedure, we cured GAP diol with propargyl alcohol and IPDI in a sequential process where GAP diol was first branched with the requisite amount of propargyl alcohol simply by blending the components and leaving the mixture overnight at 60 °C, followed by subsequent curing of the branched GAP with IPDI in the conventional manner. To distinguish this process from the standard dual curing process, where alkyne and isocyanate are used simultaneously (synchronous dual curing), we have named this process sequential dual curing.

Stress-strain curves for two test series of GAP diol samples cured using propargyl alcohol branched GAP with IPDI at two different propargyl alcohol/GAP molar ratios are summarized in Figure 6. The NCO/OH curing ratio was kept at 1.0 for both series (this includes the hydroxyl-content introduced through the branching process). As seen, the mechanical characteristics of these specimens were outstanding, comparable to and even slightly exceeding those obtained using the N100-IPDI mixture (Figure 3).

To more clearly comprehend and compare the mechanical properties obtained with the various curing systems, the median test sample has been abstracted from each test series utilizing N100, N100-IPDI, BPHQ, BPHQ-IPDI, and propargyl alcohol-IPDI systems, respectively, and then collected together in Figure 7. The superiority of the N100-IPDI and the sequential dual curing system is evident.

It is important to keep in mind that all curing systems using alkyne curing agents are forming triazoles through an exothermic reaction and can be accompanied by substantial heat flow, something which has been duly pointed out in literature [24]. We urge all users of triazole curing methodology to pay close attention to the heat flow accompanying the curing process, and high curing ratios and/or essentially adiabatic conditions must be avoided. Unlike the use of GAP-triazoles for some other purposes, such as preparation of triazole substituted GAP derivatives to tailor e.g. burning rate characteristics, when using them merely for curing the polymers, the degree of conversion is fortunately limited, typically perhaps ca. 5–15 % of available azide groups (all reactions here referring to triazole formation by alkyne treatment of GAP). In addition, for composite propellant processing, the binder system constitutes only the minor part of the propellant system, further diluting the heat flow. In any case, the sequential dual curing process reported here, unlike synchronous dual curing, is very favorable in this context because no crosslinking takes place under the triazole formation (the branching process), meaning that the propargyl alcohol can be added portion wise if needed.

3.5 Glass Transition Temperatures of Cured GAP Binder Systems

Perhaps the most frequently repeated objection to the use of polyfunctional alkynes for curing of GAP binder systems is the heightened glass transition temperatures measured in such samples compared to analogous samples cured with isocyanates. What is often forgotten is the fact that binder systems for rocket propellants are almost exclusively

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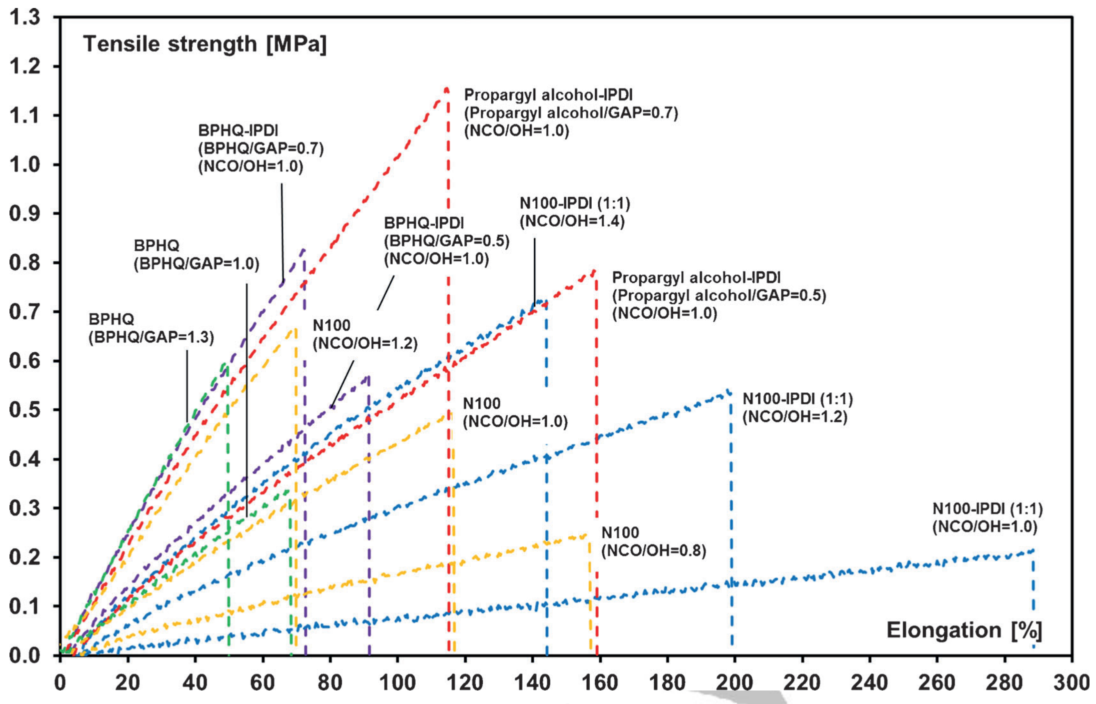

Figure 7. Comparison of the mechanical characteristics of various curing systems for GAP diol as represented by the median sample (with respect to elongation) from each test series.

plasticized, and unlike non-plasticized systems, where only polymer–polymer interactions are rendered possible, polymer–plasticizer interactions can be dominant in the analogous plasticized systems. Subsequently, few conclusions can automatically be deduced from the study of non-plasticized specimens.

We have measured the glass transition temperature (T_g) of both non-plasticized and BuNENA plasticized polymer samples using DMA (using a BuNENA/prepolymer mass ratio of 0.46). These results are summarized in Table 2.

The "equalizing" effect of the plasticizer is evident from Table 2. The T_g value of the non-plasticized sample cured with N100-IPDI isocyanate mixture was −37 °C. Both isocyanate-free curing with BPHQ and synchronous dual curing with BPHQ-IPDI gave non-plasticized samples with very similar T_g values of −36 °C and −35 °C, respectively, very similar to the isocyanate-cured sample. The non-plasticized sample prepared using sequential dual curing had a somewhat elevated T_g value of −25 °C. However, when analogous samples were plasticized with BuNENA, they all had very similar T_g values in the region of −58 °C to −55 °C. Similar values have been obtained by us with samples containing TMETN plasticizer, but this has not been comprehensibly examined. As such, the adoption of alkynes in some form of curing system for GAP propellant binders is probably not significantly hindered by the heightened glass transition temperatures of such binders. Although low temperature mechanical properties are critical for all missile applications to avoid motor failure by propellant cracking, projected areas of applications for GAP-based rocket propellants are first and foremost not those that have the most stringent requirements with respect to low temperature characteristics. Especially tough temperature conditions apply for missiles in the air-to-air domain, not the primary area of interest for GAP propellants at the moment. That said, the most challenging part of preparing smokeless, chlorine-free GAP propellants is the attainment of proper binder–filler interactions [11].

Table 2. Glass transition temperatures of non-plasticized and plasticized GAP diol samples cured with various curing systems.

Curing system	Plasticizer[a]	T_g by DMA[b] [°C]
N100-IPDI	None	−37
N100-IPDI	BuNENA	−58
BPHQ	None	−36
BPHQ	BuNENA	−55
BPHQ-IPDI	None	−35
BPHQ-IPDI	BuNENA	−57
Prop.alc.-IPDI	None	−25
Prop.alc.-IPDI	BuNENA	−56

a) The plasticizer/prepolymer ratio was 0.46 for all samples containing plasticizer. b) The glass transition temperature was determined from the peak of the loss modulus, oscillating frequency 1 Hz.

4 Conclusions

Isocyanate, alkyne, synchronous dual, and sequential dual curing systems were evaluated by uniaxial tensile testing of

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non-plasticized polymer samples in order to identify the most useful curing conditions for commercially available, linear GAP diol binder destined for solid rocket propellants. Isocyanate curing using mixed isocyanates is superior to isocyanate-free curing with BPHQ. Synchronous dual curing, employing BPHQ and IPDI simultaneously, gave samples with much improved properties in comparison with those from alkyne curing, but fell short of properties obtained with mixed isocyanate curing.

Sequential dual curing, using propargyl alcohol as a hydroxyl-telechelic branching agent for GAP diol, followed by conventional isocyanate curing, holds much promise and compares favorably to curing with mixed isocyanates. Sequential dual curing offers some advantages over orthodox curing with mixed isocyanates, such as the use of only commercially available and well-defined, monomeric species (propargyl alcohol and IPDI). In addition, some gains are achieved compared to alkyne curing or traditional dual curing (synchronous dual curing), such as a much higher degree of control over the pot-life time (the final crosslinking is completed using conventional isocyanates), as well as the safety aspects related to the exothermic and potentially hazardous triazole formation because the triazole formation precedes the final crosslinking process and can be regulated by use of portion wise admixtures (stepwise conversion) of the alkyne (propargyl alcohol) if necessary.

Compared to isocyanate curing, the glass transition temperatures in non-plasticized polymer samples were heightened when triazole-based curing methods were included, but the T_g values were nearly identical in all samples when plasticized with BuNENA, irrespective of the curing method.

Symbols and Abbreviations

ADD – Agency for Defense Development
ADN – Ammonium dinitramide
AP – Ammonium perchlorate
ASTM – American Society for Testing and Materials
BABE – Bisphenol A bis(propargyl ether)
BHPB – 1,4-Bis(1-hydroxypropargyl)benzene
BPHQ – Bispropargylhydroquinone
BPS – Bispropargyl succinate
BuNENA – *N*-butyl-2-nitratoethylnitramine
DDPM – 2,2-Bis(prop-2-ynyl)malonate
DMA – Dynamic mechanical analysis
DSC – Differential scanning calorimetry
FFI – Norwegian Defence Research Establishment
GAP – Glycidyl azide polymer
ICT – Institut für Chemische Technologie
IPD – Isophorone diisocyanate
IR – Infrared
J – Coupling constant (NMR)
N100 – Hexamethylene diisocyanate biuret trimer
NENA – Nitratoethylnitramine
NMR – Nuclear magnetic resonance
PTFE – Polytetrafluoroethylene
STANAG – Standardization Agreement (NATO)
T_g – Glass transition temperature
TMETN – Trimethylolethane trinitrate
TPB – Triphenyl bismuth
XLDB – Cross-linked double base
δ – Chemical shift (NMR)
ν – Wave number (IR)

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FULL PAPERS

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■■–■■

Curing of Glycidyl Azide Polymer (GAP) Diol Using Isocyanate, Isocyanate-Free, Synchronous Dual, and Sequential Dual Curing Systems

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