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*Research paper*

# Influence of the Prepolymer Structure of Glycidyl Azide Polymer (GAP) on Binder Properties - Some Theoretical Considerations

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**Abstract:** Glycidyl azide polymer (GAP) is a promising energetic binder for solid propellants, but it suffers from poor mechanical properties compared to hydroxyl-terminated polybutadiene (HTPB). This paper reviews the main factors affecting the mechanical properties of GAP-based binders, such as molecular weight and functionality, and discusses some possible strategies on how it could be improved. The equation of Carother is used for the theoretical consideration of the functionality of the GAP prepolymer.

**Keywords:** glycidyl azide polymer, GAP, energetic binder, propellant binders, mechanical properties

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# 1   Introduction

Polyethers containing azidomethyl side chains have been known since the 1970s [1] and the hydroxyl-terminated azide prepolymer (glycidyl azide prepolymer,

GAP) was first proposed as an energetic polymer by Rocketdyne (Rockwell). GAP is an energetic binder that is being considered to replace the inert HTPB binder to increase the performance of composite propellants [2, 3]. Glycidyl azide polymer (GAP) is a hydroxy-terminated polyether with azide groups in the side chain, and with a polyether structure in the backbone.
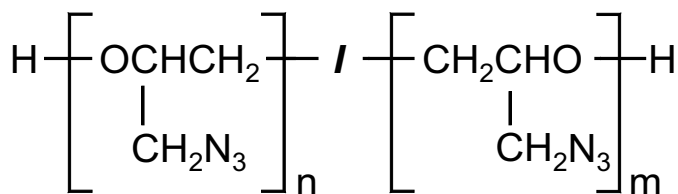
$$H\left[OCHCH_2\atop \quad\ \ CH_2N_3\right]_n I \left[CH_2CHO\atop \quad\ \ CH_2N_3\right]_m H$$

**Figure 1.** General structure of GAP-diol ($I$ = diol initiator, $n \geq 1$, $m \geq 1$)

This energetic prepolymer has advantages, such as a positive heat of formation and high density, making it a promising candidate for binders for next-generation solid propellants. However, it suffers from poor mechanical properties compared to hydroxyl-terminated polybutadiene (HTPB). Although GAP has been known for a long time, no applications in rocket propellants are known. Many researchers have investigated GAP [4-15] as a binder in propellant formulations but have encountered problems in achieving the desired mechanical properties. The problem becomes more and more severe as the filler content of a propellant is increased.

When using glycidyl azide binders in propellants, the chemist typically face the following challenges:
– insufficient mechanical properties,
– high glass transition temperature (cured GAP binder ~ –35 °C),
– filler-binder interactions,
– high mixing and casting viscosities during processing, which limits the maximum filler content,
– low reactivity during curing due to the secondary hydroxyl groups, which can cause side reactions if traces of water are present in the formulation, and also problematic curing when chain extender/crosslinking triols with primary hydroxyl groups are used,
– solubility of energetic filler in polar binders,
– price.

One of the major challenges is the realization of good mechanical properties of a propellant. The mechanical properties of a rocket propellant are determined by the binder network, the amount of filler and the binder/filler interaction.

GAP is often compared to HTPB, especially in term of the propellant properties [14]. Both are cross linked using isocyanate. In the present paper, the fundamental differences between the two prepolymers are compared and their network structure is discussed by considering a few theoretical considerations. Possible side reactions such as the formation of allophanate [16] or tetrazolin-5-one [16, 17] are not considered because the authors were only able to observe such reactions in their previous work under conditions that do not normally occur during propellant production [18].

In many of the publications, GAP diol with a number average molar mass ($M_n$) of 2000 g/mol is used for preparing the binder network. GAP with other molar masses are also reported in the literature (Table 1). Information on these prepolymers and their commercial availability or resulting binder properties is very limited. GAP is typically produced on a small scale by several research centres. To the best of the authors' knowledge, not many GAP types with an OH functionality of exactly two are known to deserve the name GAP-diol, *e.g.* such a difunctional GAP can be expected from the data given in [14]. Reference [19] mentions the functionality of 2.0 for a GAP-diol but Mn, equivalent weight and functionality are contradictory. In the present GAP-(x)ol is used to describe the number of OH groups per prepolymer chain. X is defined by the hydroxyl functionality of the prepolymer chain. Table 1 shows a selection of the GAP-(x) ol types found in the literature, sorted by country.

Research on GAP propellants is still active. A GAP-based propellant has been considered for minimum smoke propellants for tactical missiles by different companies. It is difficult to find out from the literature whether these are in operational use or not. At least Safran has published GAP-based formulations under the tradenames Azamite®R, Azamite®C, and Azalane®HMX for medium range missile, which are expected to be deployed within the French armed forces in 2025 and antitank missiles expected in 2023 [36, 37].

**Table 1.** Properties of some GAP-(x)ol samples from commercial and non-commercial sources

| Country | Producer | Sample type | Mn [g/mol] | Equivalent weight OH [g/mol-eq] | Functionality f = $M_n$/eq. weight OH |
|---|---|---|---|---|---|
| France | Eurenco | GAP Diol | 1400-2000 [19, 20] | 1000-1400 [19, 20] | 1.4-1.6[f] |
| | | GAP Triol | ≥ 900 [19, 20] | ≥ 400 [19, 20] | 2.5-3.0 [19,20] |
| USA | 3M | GAP polyol 5527 | 5000-6000 [2, 3] | 2000 [21] | 2.5-3[f] |
| | | – | 5500 [22] | 2040 [22] | 2.7[f] |
| | | GAP diol L9961 | 2400 [22] | 1351 [22] | 1.8[f] |
| Japan | a) | NOF-9D535 | 2256 [23] | e) | e) |
| China | b) | – | 3600 [24] | 1818[f] | 1.98[f] (2.04 [24]) |
| | k) | – | 3600 [25] | 1888[f] | 1.9[f] |
| | c) | – | 2000 [26] | 684.4[f] | ~2.9[f] |
| | c) | – | 4000 [27] | 1961[f] | ~2.0[f] |
| | c) | – | 3400 [28] | 1618[f] | ~2.1[f] |
| | b) | – | 3700 [29] | 1924[f] | ~1.9[f] |
| India | j) | – | 2138 [30] | 1014 [30] | 2.1[f] |
| Poland | d) | – | 4500 [31] | 1753 [31] | 2.6[f] |
| Russia | g) | – | 1300 [32, 33] | e) | e) |
| Canada | h) | Linear GAP[i] | 3000 [34, 35] | ~1500[f] | ~2 [34, 35] |
| | | Branched GA[Pi] | 4500 [34, 35] | e) | >2 [34, 35] |

a) NOF Corporation - Nippon Oil & Fats Co., Ltd,
b) Liming Research Institute of Chemical Industry, Henan
c) 42 Institute of the Fourth Academy of China Aerospace Science and Technology Corporation
d) Warsaw University of Technology, Department of High-Energetic Materials
e) No data available
f) Values calculated by the present authors
g) Semenov Institute of Chemical Physics, Moscow
h) Defense Research Establishment, Val Cartier
i) It is not clear from [34, 35] whether these were really synthesized at h).
j) Vikram Sarabhai Space Centre (VSSC)
k) Hubai Aviation Institute of Chemical Technology

## 2   Discussion

The requirements of modern rocket propellants place high demands on the quality of the binder network. A binder with good mechanical properties requires a low modulus and high elongation and therefore a low crosslink density or long chains between the crosslinking points. The modulus of the binder is directly proportional to the crosslink density, while the elongation is inversely related to it.

Energetic polymers are created by attaching energetic groups to a polymer chain. However, pendant groups also affect the properties of the polymer, such as melting point, low temperature flexibility, glass transition temperature, and crystallinity. In addition, pendant groups reduce the effective chain length between the crosslinks and do not contribute to the mechanical properties of the binder network, because the molecular weight of the chain between the crosslinks ($M_c$) is reduced and is considerably lower than the molecular weight of the repeating unit ($M_n$). In other words, the higher the $M_c/M_n$ ratio the higher the number of macromolecular chains that form the network and contribute to strengthening its mechanical properties. Only "effective" chains are responsible for the binder network. A chain is effective if it has at least two points of attachment to the binder network, preferable at the ends of the chain, otherwise it will not contribute to the mechanical properties. To obtain the most effective network, all ends of the prepolymers should be linked to the network (Figure 2), avoiding both cyclic loops and unconnected dangling chain ends (Figure 3), and this can only be achieved with telechelic polymers.
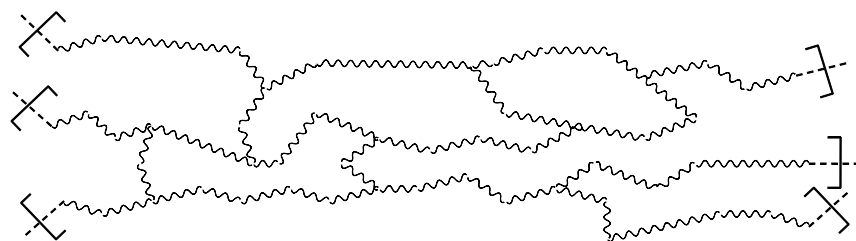


**Figure 2.**   Desired network with di- and tri-functional linkages, where all prepolymer chains contribute to the mechanical properties
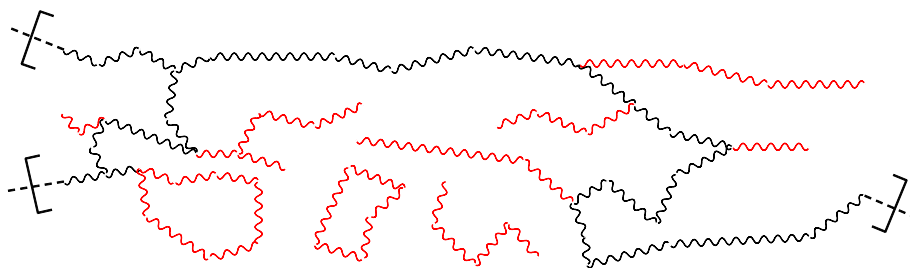
**Figure 3.** Incomplete network with free chain ends of monofunctional polymers, loops and oligomers

In the case of GAP, azide side groups are attached to a backbone chain and thus the effective chain length is lower than deemed by its molecular weight ($M_c < M_n$). Obviously, for the same molecular weight, prepolymers with pendant groups (GAP) have a much shorter chain length than the (almost exclusively) straight chain polymers such as HTPB. The ratio of non-load-bearing pendant groups to the mechanically effective part of the chain is often quite considerable. For GAP, 44 wt.% of the monomer unit ($C_3H_5N_3O$) contributes directly to the mechanical strength; 56 wt.% of the molecular weight does not contribute directly to the mechanical strength of the binder because it is involved in forming the pendant azidomethyl side groups ($CH_2N_3$). For comparison, only 10 wt.% of Poly bd R45-M is involved in forming the pendant vinyl groups.

The two prepolymers can be compared by calculating the molar masses of GAP-diol and HTPB required to have comparable chain lengths between the cross-linking points. The first calculation determines the corresponding molecular weight of a GAP prepolymer using an HTPB typically used in military missiles. The molecular weight ($M_n$) of Poly bd R45-M resin [38] is 2800 g/mol. This HTPB uses 2520 g/mol to build up the chain length. In order to obtain a GAP with a comparable chain length, the prepolymer requires a molecular weight of ~5700 g/mol. The second calculation takes the $M_n$ of a commercially available GAP, assumes that it is HTPB, and computes a comparable GAP. The commercially available "GAP-diol" from Eurenco [19, 20] has a mean number molecular weight of about 2000. But to be comparable to HTPB with the same mean number molecular weight of 2000 it needs a molecular weight of ~4100 g/mol to build up the same chain length. This difference has two main effects on the binder. Firstly, the length of the polymer segments between cross-link junction points is shorter for GAP compared to HTPB, and as a result, the cured GAP network is less elastic. Secondly, a larger amount of binder is required in the propellant formulation to obtain the desired propellant properties.

In principle, a higher amount of GAP binder is not necessarily a disadvantage, as it is with inert binders, since the maximum specific impulse is achieved with less filler content. However, a higher binder content should at least have a positive effect on the mechanical properties of the propellant.

Beside the length of the polymer chains as described by $M_c$, the functionality is an important parameter for a prepolymer. Ideally it should be two for hydroxy-terminated prepolymers. This determines the number of cross-links per $M_n$, and if the value is less than 2, the number of unconnected dangling chain ends is increased. Dangling chains reduce the extensibility of the binder network if significant numbers are present in the polymer. It is important to know the exact functionality and functionality distribution of the prepolymer; unfortunately only a number average functionality can be determined [39], and this gives only a statistical overview. Most of the functionalities reported by the manufacturers of prepolymers are the ratio of the number average molecular weight ($M_n$) to the equivalent weight. Such data can be misleading. The commercially available "GAP-diol" from Eurenco, has a functionality of around 1.6. How this factor interferes with the formation of an ideal network structure as can be considered theoretically by using Carothers' equation [40]. Carothers relates the functionality ($f$), the extent of reaction ($p$), defined as the fraction of functional groups/monomers that have reacted and the average number of repeating units. This is illustrated by the following example where difunctional GAP and a difunctional curing agent react in the presence of monofunctional GAP. The resulting chain length of the polymer backbone will be shorter when GAP-ol is present. The effect of the functionality of the prepolymer on the length of the polymer chain can be described by the following equation (Carothers' equation):

$$\bar{X}n = \frac{r + {}^{f}/_{2}}{2r + f - 2rpf}$$

where  is the  average number of repeating units in the polymer, $r$ is the molar ratio of curing agent groups to –OH groups, $f$ is the average functionality of the prepolymer containing –OH groups and $p$ is the extent of reaction.

**Table 2.** Dependence of repeating units on functionality, ratio, and extent of reaction

| Functionality $f$ | Ratio curing agent groups/OH groups $r$ | Extent of reaction $p$ | Repeating units |
|---|---|---|---|
| 2 | | 1 | ∞ |
| 1.9 | | 1 | ~20 |
| 1.6 | | | ~5 |
| 2 | | 0.95 | 10 |
| 1.9 | | 0.95 | ~7 |
| 1.6 | 1 | | ~3 |
| 2 | | | 5 |
| 1.9 | | 0.90 | ~4 |
| 1.6 | | | ~3 |
| 2.1 | | 0.95 | 18 |
| 2.1 | | 0.90 | ~6 |
| 2.2 | | 0.95 | 105 |
| 2.2 | | 0.90 | ~9 |
| 2.2 | 0.90 | 0.95 | ~8 |
| 2.3 | 1 | 0.90 | ~13 |
| 2.4 | | | ~28 |

At a reactant ratio of one, assuming complete reaction, the chain length expressed by the repeating units is infinite if no monofunctional material is present and decreases dramatically if the functionality is decreased. For example, for a GAP with a poor $f$ of 1.6 the presence of monofunctional units in the prepolymeric GAP-(x)ol is obvious when looking at the functionality. Intentional or incidental chain termination occurs after ~5 repeating units and the formation of dangling chains occur. Dangling chain ends do not contribute to the polymer network and negatively affect the mechanical properties. In comparison, HTPB (*e.g.* Poly bd® R-45M $f$ = 2.2-2.4 [2, 3]) will form a network with a higher number of repeating units between the crosslinking points, resulting in better binder properties. This can be seen clearly in Figure 4. The graph shows the dependence of the repeating units on the functionality at different OH ratios and the extent of reaction calculated with Carothers' equation. The diagram shows that the greater the deviation from the ideal reaction, the greater the functionality required to form long chain polymers. Conversely, a polymer with a functionality less than 2 needs a curing agent with a functionality greater than 2 to be able to form longer chains or even a network.
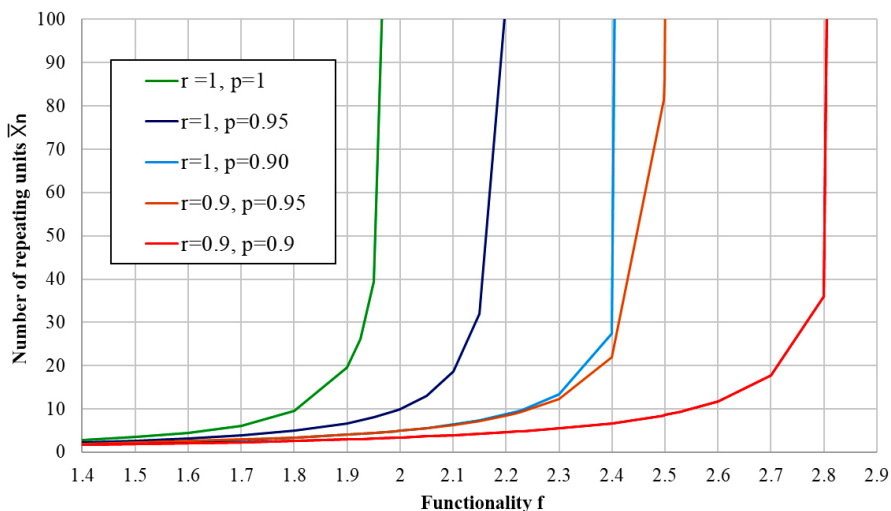
**Figure 4.** Dependence of the number of repeating units on functionality for different *r* and *p* values

The different functionalities of GAP and HTPB are the reason why they need to be cured in different ways. HTPB R45 can be cured with difunctional isocyanates. This is not possible for GAP-(x≤2)ol. It would result in a linear polymer with very poor dimensional stability, especially at the upper end of the required temperature range. In the case of GAP-(x≤2)ol, interchain linkages must be provided by a curing agent. Either by using a mixture of difunctional and a high amount of higher functionality isocyanate, by the addition of a higher functionalized alcohol, or by linking a few azide groups. Various curing methods have been published on the curing of GAP-(x)ol and GAP propellants using isocyanate, isocyanate-free, synchronous dual and sequential dual curing systems [14, 15]. However, all of these curing methods cannot solve the fundamental problems of short effective chain length and low functionality of GAP. Linking all short chains and dead-end chains through the azide groups would result in a more crosslinked polymer, which would result in poor elastomeric properties. To obtain an elastomeric network with a wide-meshed structure from low-functional (<2) prepolymers, a dual curing method can be used. This process involves chain extension by reaction with an appropriate mixture of di- and higher functionalized isocyanate curing agents and a limited crosslinking of the resulting linear chains via azide groups. Regardless of the curing method used, it will always be difficult or impossible to achieve the desired mechanical properties in a propellant formulation from a low-functional (<2) prepolymer.

Another important aspect is the degree of polymerization, which can be seen in Table 2. At a lower degree of polymerization ($p < 1$), the effect of functionality is not negligible. The chain length decreases from infinity to 10 for a prepolymer with an "ideal" functionality $f = 2$ by lowering the extent of reaction to $p = 0.95$, but for $f > 2$ at the same extent of reaction ($p = 0.95$) the number of repeating units is much higher.

A decrease in the extent of the reaction leads to a decrease in the number of repeating units. However, this can be counteracted by increasing the functionality, which then leads to a higher number of repeating units, but also to a higher degree of crosslinking due to the higher functionality. According to Table 2, long linear chain segments between connecting points, which should result in a binder network with proper mechanical properties, could be achieved with a functionality of 2.2.

From the above considerations, it is clear that to achieve the desired mechanical properties for rocket propellants, one needs a GAP-(x)ol with a functionality of 2 per prepolymer unit or slightly more, combined with a molecular weight of the prepolymer ($M_n$) of more than 4100 g/mol to ensure a sufficient chain length or Mc between the connection points. GAP types found in the literature with a functionality of 2 or more will not really solve the problem because the published functionalities are average functionalities and contain an undefined amount of low-functional ($<2$) prepolymers, which will lead to the described network defects.

A GAP produced commercially by 3M [21], a GAP from Liming Research Institute of Chemical Industry [24] and a GAP synthesized in Poland by Chmielarek *et. al.* [31] appears to partially meet these requirements. Unfortunately, there is no general availability due to known restrictions and hardly any data is publicly available. It is therefore difficult to assess whether a GAP (x)ol type listed in Table 1 has the desired properties. At least those with higher molecular masses have functionalities greater than 2. But the fraction of the functional groups available for the crosslinking (($f$-2)/$f$) of these higher molecular weight prepolymers appears to be too high for an elastomeric network [41].

Higher molecular weight usually means a higher viscosity. For GAP this is not quite as dramatic because a significant amount of plasticizer is needed to lower the high glass transition temperature ($T_g$) of the cured GAP binder (approximately –35 °C). This will also lower the viscosity and improve the processability, but at higher plasticizer concentrations a higher crosslink density is required to achieve proper curing, which complicates the tuning of propellant properties, especially if the optimal prepolymer is not available. This illustrates the next major difference between GAP and HTPB. While the plasticizer in HTPB

is more of a processing aid, the GAP binder requires a significant amount of plasticizer to meet the requirements for air launched rockets (*e.g.* $T_g = -54$ °C). To lower the $T_g$ of the GAP binder, an energetic plasticizer should ideally be used so that the energy gain from the active binder is not reduced. In addition to linear GAP, branched GAP is also described in the literature, which has a lower $T_g$ and suitable functionalities, but no data on binder properties are available [34, 35].

If GAP is cured by isocyanates together with a crosslinker or chain extenders that carry primary hydroxyl groups, it should be considered that GAP carries predominantly secondary hydroxyl groups [22, 42-45]. The lower reactivity of the secondary hydroxyl group makes reproducible curing with higher functional alcohols more difficult, as these usually carry primary hydroxyl groups. Therefore, it may also be advantageous to have telechelic prepolymers with primary [46] instead of secondary OH groups.

## 3    Conclusions

♦ The effective chain length of the prepolymer and the degree of crosslinking are the main factors influencing the mechanical properties. This paper describes the main reasons why it is difficult to achieve similar binder properties as HTPB R45 with the GAP prepolymers currently known or described in the literature.

♦ The use of GAP prepolymers with short chain length and low OH-functionality, or prepolymers with longer chain length and too high functionality, or prepolymers with an average functionality of about 2, leads to the formation of dangling chains or tighter crosslinking and the formation of an inadequate elastomeric network with reduced elasticity.

♦ To overcome this drawback for the prepolymeric glycidyl azide polymer, a functionality of at least two for each unit of the prepolymer and a longer chain length is required. The latter requires a higher effective molecular weight to compensate for the reduced $M_c$ by the azidomethyl side groups.

♦ Results from calculations using Carothers' equation showed a strong dependence of the number of repeating units at different extents of reaction and OH/NCO ratios on the functionality of the prepolymer when cured with a difunctional curing agent. A useful compromise could be a functionality of around 2.2 Thus, a prepolymer should have a linear structure with terminal functional groups and some additional functional groups in the side chain of the prepolymer to realize a functionality of about 2.2 . To obtain chain length between the crosslinking points similar to the widely used HTPB R45,

an effective molecular weight requires a GAP prepolymer with a molecular weight of at least 4100 g/mol. This should help to achieve mechanical properties which are comparable to those of HTPB R45.

♦   It is up to the chemist to synthesize a suitable prepolymeric GAP that meets the criteriamentioned. However, until this is done, it will remain a challenge to achieve the desired properties of a rocket propellant with a glycidyl azide polymer binder.

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