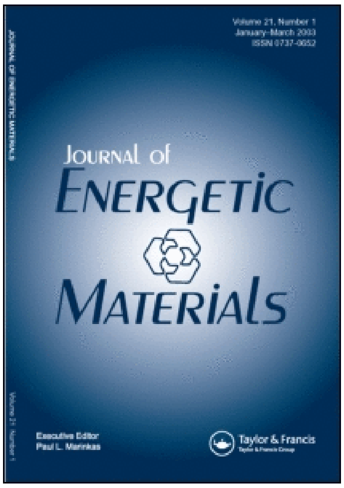

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GLYCIDYL AZIDE POLYMER (GAP) - AN ENERGETIC COMPONENT OF ADVANCED SOLID ROCKET PROPELLANTS - A REVIEW

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ABSTRACT

This paper reviews physico chemical, thermal, mechanical and ballistic characteristics of glycidyl azide polymer (GAP) and GAP based solid propellants. GAP offers propellant system with superior ballistics and high performance. Its potential as an energetic additive is attributed to the highly exothermic scission of $-N_3$ bond structure accompanied by the release of energy of the order of 685 kJ/mole. Inclusion of GAP in propellant compositions leads to an improvement in their mechanical properties.

INTRODUCTION

Glycidyl azide polymer (GAP) offers an unique energetic binder and plasticizer system for advanced propellants and plastic bonded explosives (PBX) for achieving higher performance, superior structural integrity and low vulnerability. Its chief advantages are higher density and

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positive heat of formation as compared to widely used binder, hydroxy terminated polybutadiene (HTPB) and non-explosive plasticizer, diethyl phthalate (DEP) (1,2). Its potential to offer higher energy in spite of low concentration of oxygen is attributed to the scission of azide bond structure $-N_3$ to $-N_2$ (3). GAP contains relatively higher concentration of 'C' atoms and therefore its high combustion potential could be exploited by the inclusion of oxidizers (4). Owing to its unique thermal decomposition behaviour, GAP itself can burn at elevated temperatures and pressure (> 0.3 MPa) without any oxidizer, thereby offering a monopropellant and as fuel in the primary combustor of ducted rockets (5). Further it is expected to produce chlorinefree propellants which are in great demands due to tremendous pollution hazards of AP-based propellants, which may be realized from the fact that a single launch of USA space shuttle results in exhaust of 220 tons of HCl (5).

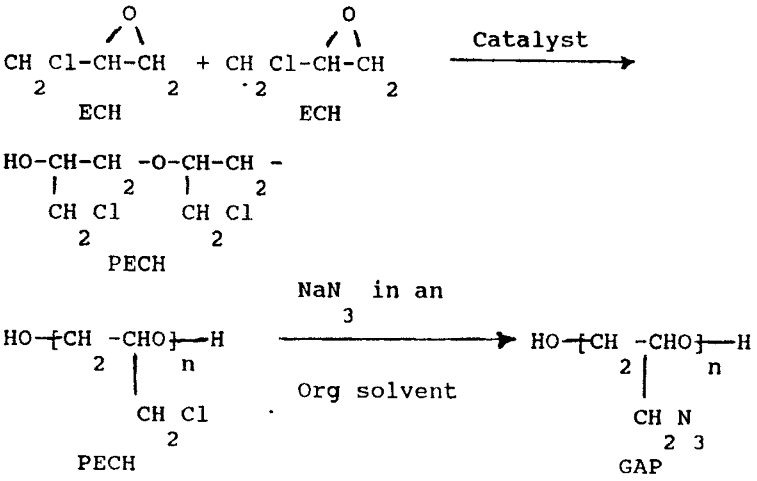
The main demerits of GAP are relatively high glass transition temperature (T_g) $- 43\,^{o}C$ and low weight percentage of polymer weight bearing chain (6). High molecular weight

GAP are generally preferred to overcome the latter problem. This paper reviews the work done so far on GAP with emphasis on its potential for usage as binder/plasticizer/additive for high energy solid propellants.

SYNTHESIS OF GAP

A number of methods are reported for the synthesis of GAP during last decade(5,7-10). In general, GAP can be prepared by two different methods involving two step and one step processes.

The two step process includes polymerization of epichlorohydrin (ECH) to Polyepichlorohydrin (PECH) using suitable catalyst. Subsequently, PECH is



$$\underset{\text{ECH}}{CH_2Cl-CH\overset{O}{-}CH_2} + \underset{\text{ECH}}{CH_2Cl-CH\overset{O}{-}CH_2} \xrightarrow{\text{Catalyst}}$$

$$\underset{\text{PECH}}{HO-\underset{CH_2Cl}{\underset{|}{CH}}-CH_2-O-\underset{CH_2Cl}{\underset{|}{CH}}-CH_2-}$$

$$\underset{\text{PECH}}{HO-\left[CH_2-\underset{CH_2Cl}{\underset{|}{CHO}}\right]_n-H} \xrightarrow[\text{Org solvent}]{NaN_3\text{ in an}} \underset{\text{GAP}}{HO-\left[CH_2-\underset{CH_2N_3}{\underset{|}{CHO}}\right]_n-H}$$

converted to GAP in an organic or aqueous solvent (11,12). The one step method yielding GAP of low molecular weight (~500) involves direct conversion of ECH to GAP (13).

The conversion of ECH to GAP is confirmed by the appearance of sharp band of $-CH_2N_3$ at 2100 cm^{-1} and total disappearance of $-CH_2Cl$ band at 720 cm^{-1}, in IR spectra. ^{13}C NMR, mass spectra and elemental analysis have been used for the characterization of GAP (5).

PHYSICO-CHEMICAL PROPERTIES OF GAP

As in the case of other polymers, the physico-chemical properties of GAP can not be absolute and they differ mainly as the degree of polymerization,structure and method of preparation changes. Physico-chemical characteristics as reported by various researchers are given in Table 1.

THERMAL DECOMPOSITION STUDIES ON GAP

Kubota (3) carried out DTA and TG studies on GAP under helium atmosphere (0.1 MPa) at heating rate of 0.167 K/s. They attributed the exothermic peak observed between 202 and 277 °C to decomposition and gassification reactions.

This exothermic peak corresponds to first stage weight loss of 40% in TG. The second stage weight loss in TG began at $277\,^{\circ}$C without heat liberation. In order to understand the decomposition pattern they had undertaken interupted DTA - TG studies and DSC experiments. On the basis of results obtained they have established that the initial decomposition of GAP is caused by the degradation of molecular structure $-CH_2-N{=}N_2$ to $-C \equiv N + N_2 + H_2$. This decomposition is highly exothermic corresponding to the release of 685 kJ/mole energy. Succeeding decomposition of the acrylonitrile molecular structure liberates carbon and oxygen atoms.

Farber et al (14) in mass spectroscopic studies observed primary decomposition at $120\,^{\circ}$C with activation energy of 42.2 kcal/mole. Secondary decomposition involving rupture of carbon backbone was recorded at $200\,^{\circ}$C. Leu et al (15) have carried out detailed DSC and TG studies and observed first stage decomposition at $240\,^{\circ}$C and second stage degradation at $260\text{-}500\,^{\circ}$C. Oyumi and Brill (16) have reported real-time, high-rate, variable-pressure thermolysis results on GAP. The products of decomposition were characterised by using rapid scan fourier transform infrared spectroscopy (RSFTIR). The experiments carried out at atmospheric pressure recorded the onset of decomposition at 215 °C by the appearance of peaks at 1630-1730 cm^{-1}. The intensity of these peaks increased while the azide peak intensity diminished as the decomposition progressed. The new absorptions were also recorded in the 3300-3400 cm^{-1} and 1600-1650 cm^{-1} range.The spectral features of the polymer backbone remained essentially unchanged after the disappearance of the azide group. The overall product analysis results establishing HCN as a major decomposition product were in close agreement with those reported by Flanagan et al (17) using GC-MS for product characterisation.

Accelerated rate calorimetry (ARC) of GAP carried out by Mishra et al (6) in conjunction with DSC, revealed onset of exothermic decomposition of GAP at 217-218 °C. Energy of activation of about 38.23 kcal/mole has been reported by these workers. Stability of 23 min for GAP in a 500 ml flask at 166 °C and 23 d in a 10000 gallon tank at 108 °C has been recorded by these researchers.

Mishra et al (18) have also studied the pyrolysis products of GAP at 250, 500, 750 and 2000 ^{o}C by using gas chromatography and mass spectroscopy. They concluded that N-atom's loss is the preliminary step in the decomposition of GAP.

GAP BINDER

Leu et al (15) found in DSC studies that the heat of formation of GAP (474 cal/g), decreases to 443-454 cal/g on addition of 25-30 % nitroplasticizers like BDNPA/F (Bis dinitro propanol - Acetal/formal) and then increases to 483 cal/g on addition of 50 % nitroplasticizer. In TG, three stage weight loss reactions were observed at 493, 518 and 543-773 ^{o}C. The main limitations of nitroplasticizers is depletion of stabilizer at faster pace on prolonged exposure. Tokui et al (5) have evaluated mechanical properties, swell ratio and sol fraction of GAP binder using various curatives, plasticizers and trimethylol propane (TMP) as crosslinker. They found that triphenyl methane triisocyanate and polymethylene polyphenyl isocyanate reacted with GAP too rapidly and Sumidur-N (triisocyanate) yielded poor mechanical properties. Hexamethylene diisocyanate (HMDI), toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI) having decreasing order of reactivity reported to be promising. Among them IPDI was found to be the best, giving binder with superior mechanical properties. T.S. 29 kg/cm^2, % E 250~600%, swell ratio Q-7 and sol fraction S-15%

In order to improve upon the poor mechanical properties of GAP binder at low temperature (T_g $-43^{o}C$) various plasticizers namely, iso decyl pelargonate (IDP), dioctyl adipate (DOA), dioctyl azelate (DOZ), dioctyl sebacate (DOS) and diethyl phthalate (DEP) were investigated. DOS, DOZ and DOA are reported as good plasticizers. However, DOZ like BDNPA/F decreases the tensile strength and retards the curing reaction between GAP and IPDI. IDP causes plasticizer and antioxidant bleeding. Stacer et al(2) have studied various binder systems and reported that GAP gives superior burning rates (16-18 mm/s) alone and in combination with triethylene glycol dinitrate (TEGDN) than HTPB (6-7 mm/s), CTPB (11-16 mm/s), polymethyl acrylate (PMA), polydiethylene glycol adipate (PGA) (3-7 mm/s) and poly dimethyl siloxane (PDMS) (15 mm/s). However, GAP based binder recorded the highest temperature sensitivity σp (40 $K^{-1} \times 10^{-4}$) in comparison with the other binders studied (9-25 $K^{-1} \times 10^{-4}$). The density and thermal expansion coefficient αf of GAP (1.3 and 7.57) respectively were higher than that of the other binder systems, while linear expansion coefficient were comparable (~ 1). Decomposition temperatures of GAP and GAP/TEGDN binder (245 and 200 °C respectively) were considerably lower than that of other binder systems (>300 °C). These researchers have established direct relation-ship between burning rate and decomposition temperature of binder composition (2).

GAP BASED PROPELLANTS

Kubota and Sonobe (19) have reported that GAP propellants offer high burn rates eventhough the energy within a unit mass of propellant is relatively low. These researchers have found that the burning rate depends largely on the initial temperature and the concentration of GAP.

DOUBLE BASE PROPELLANTS

Nakashita and Kubota (20) have carried out detailed investigations on GAP based double base propellants. They reported low flame temperature (1092 K) and high burning rates (10.7 mm/s) of GAP as compared to DBP (2443 K and 6.9 mm/s respectively). However, GAP produces higher temperature sensitivity. The activation energy of decomposition of burning surface of GAP propellants is calculatd to be 87 kJ/mole.

They have also reported that on replacement of 12.5 % DEP in DB propellants by GAP burning rate is increased by 100% at 50 KSC and there was a straight line relationship between log of burning rate and pressure. They found replacement of DEP by GAP tends to increase adiabatic flame temperature and Isp.

Our studies on slurry cast GAP based double base propellants revealed an increase in cal-val and burning rates on incremental replacement of DEP by GAP. However, replacement of NG by GAP (upto 8% level) resulted in decrease of both the parameters(21).

COMPOSITE MODIFIED DOUBLE BASE (CMDB) PROPELLANTS

Sayles(22) has patented a non-NG CMDB composition based on GAP. The patent describes the properties of GAP compositions containing NC 12 %, GAP 24.5 %, AP 23.7 %, Al 7.3 % and other additives including non-explosive plasticizer 32.5 %. The GAP based compositions yielded ~ 35 % higher burn rates and improvement in Isp by 4 s as compared to NG containing CMDB composition.

COMPOSITE PROPELLANTS

Kubota et al (4) have carried out studies on AP, HMX and triamino guanidine nitrate (TAGN) based composite propellants. They observed that the burning rate of GAP propellants decreased with increase in weight fraction of energetic materials. Same trend was observed for pressure exponent, except for AP where pressure exponent (n) increased upto 0.1 weight fraction and then it decreased. The temperature sensitivity decreased monotonically in all the cases. Maximum burning rates were obtained at 0.1, 0.2 and 0.6-0.8 weight fraction of AP, TAGN and HMX respectively. Leu et al (15) have evaluated 80 % HMX based propellants, using GAP-BDNPA/F and HTPB binder. Each binder gave two distinct weight losses. Decomposition temperature for all compositions was higher than that of GAP alone. GAP based compositions gave higher heat of explosion than HTPB based composition. It was observed by these research workers that maximum reaction temperature (T_m) for compositions with coarse HMX,was higher than that for fine grade HMX. while medium sized HMX gave initial and maximum reaction temperature (To and Tm respectively) close to that of fine HMX. In HTPB binder system T_o and T_m are same for both coarse and medium HMX.

Tokui et al (5) have studied 59-62.5 % AN based GAP compositions. The pressure exponent (n) values of these compositions was 0.7. The composition with 62 % AN gave unstable combustion on ballistic evaluation in rocket motor.

COMBUSTION MECHANISM OF GAP PROPELLANTS

Kubota (3) have found that flame structure of GAP propellants is similar to that of DB propellant comprising of foam, fizz, dark and luminous zones. This may be due to the fact that the major products of decomposition i.e. N_2, H_2, CO and CO_2 are similar in both the cases. The high burning rate may be resulting from the fact that GAP decomposes exothermally at propellant surface. Nakashita and Kubota (20) found that reaction time in dark zone for NC/NG/GAP propellants is about 25% less than that for NC/NG/DEP propellants leading to increased temperature in the fizz and dark zones. These factors may be responsible for high burning rates of GAP based propellants.

Kubota et al(4) have studied the effect of addition of energetic crystalline materials on the burning rate characteristics of GAP propellants. The energetic particles burn as monopropellants as their decomposition products interact with the products of GAP based matrix. HMX and TAGN particles melt and gassify to form homogeneously mixed reactive gases above the burning surface of GAP/HMX and GAP/TAGN propellants.Thus the gas phase structures of GAP/HMX and GAP/TAGN propellants appears to be homogeneous. As the concentration of HMX increases the luminous flame produced above the burning surface approaches the burning surface itself. Consequently the heat flux transformed back from gas phase to burning surface increases as weight fraction of HMX increases. Since the decomposition products of TAGN are similar to HMX, it exhibites similar burning rate behaviour.

The flame structure of GAP propellants is altered by addition of AP, as oxygen rich decomposed gases of AP interact with fuel rich products of GAP, thereby producing heterogeneous gas phase structure. Maximum flame temperature was obtained with 75% AP. It increased monotonically with HMX and remained constant for TAGN till 65% level but then increased.

SENSITIVITY ASPECTS

Mishra et al (6) have reported the impact, friction and electro sensitivity aspects of GAP, TAGN, GN and AN based compositions.

Sayles (22) has reported lower impact sensitivity of GAP based propellants. Our studies have also established that GAP reduces the sensitivity of DB as well as that of AP and RDX based CMDB propellants (23).

GAP offers an unique energetic polymer system. However, limited information is available regarding various aspects of GAP based compositions. Detailed studies need to be carried out to fully exploit the tremendous potential of GAP based solid propellants. The combustion flame structure of GAP based composition is required to be systematically investigated.

TABLE 1 PHYSICO CHEMICAL PROPERTIES OF GAP

		Ref.
Molecular weight (m)	500-5000	9,22
Density (ρ)	1.3 g/cc	20,22
Viscosity (η)	500-5000 cps	9
Adiabatic flame temperature	1200 °C at 5 MPa	1
Glass transition temp (T_g)	Linear -20 to -50 °C	9,22
	Branched -60 °C	9,13
Functionality	Linear 1.5-2	9,13
	Branched 5-7	9,13
Bond energy per azido group	90 kcal/mole or 378 kJ/mole	1
Heat of formation	Linear +28.4 kcal/mole	3
	Branched +42kcal/mole	14
Heat of combustion	5010 ± 15 cal/g	9,13
Energy of activation	42 kcal/mole	14,18
Impact sensitivity	300 kg-cm	22
Weight percent in polymer weight-bearing chain	40	6
Theoretical elemental analysis	(wt.%) C H N O 37 05 42 16	-
Decomposition products :	Nitrogen, methane, ethane, ethylene, water, CO_2, propane, benzene, pyrole, furan, pyridine, HCN, acetaldehyde, ethylene oxide, acetonitrile, formamide, acetone, acetamide, propylene oxide, butadiene etc.	1,3 18,20

TABLE 2 THERMAL PROPERTIES OF GAP BASED COMPOSITION

Sr. No.	Composition	Thermal Expansion Coefficient αf-10^{-4} x k^{-1}	Initial Reaction Temp Ti ^{o}C	Maximum Reaction Temp Tm ^{o}C	Decomp. Temp. Td ^{o}C	Heat of Combustion cal/g	Heat of Explosion cal/g	Ref.
1.	HTPB+IPDI/DDI/ IPDI+DOA	2.2-3.6	-	-	324-374	-	-	2
2.	GAP+IPDI	7.6	233	240	245	4063	-	2,15
3.	GAP+TEGDN	5.4	-	-	200	-	-	2
4.	HTPB+HMX 20 % 80%	-	280	281	-	3068	809	15
5.	GAP+HMX 20% 80%	-	279	283	-	2611	1113	15
6.	GAP+BDNPA/F+HMX 10% 10% 80%	-	246	282	-	2926	1001	15

TABLE 3 COMPARATIVE DATA ON MECHANICAL PROPERTIES OF GAP AND GAP BASED COMPOSITIONS

Sr. No	Composition	Tensile strength kg/cm^2	% Elongation	Swell Ratio Q	Sol Fraction S%	Glass transition temperature T_g °C	Density g/cc	Ref
1.	HTPB+DOA+IPDI/ DDI	-	-	-	-	-80 to -88	0.92	2
2.	GAP+IPDI	29-30	250-600	6.9	15.4	-43	1.27	2,5
3.	GAP + HMDI	19.8	176	5	20.5	-	-	5
4.	GAP + TDI	17-22	184-220	5.4-6	25-35	-	-	5
5.	GAP+Sumidur N	15-25	60-86	4-5.5	22-38	-	-	5
6.	GAP+TEGDN	-	-	-	-	-70	1.27	2
7.	NG based CMDB propellant	25	54					22
8.	GAP based CMDB propellant	31	60					22
9.	GAP+AN	7	9				1.36	6
10.	GAP+PEG+AN+GN	10	14				1.3	6

TABLE 4 BALLISTIC PROPERTIES OF GAP BASED COMPOSITIONS

Sr. No	Composition	Burn rate mm/s @ KSC	Pressure Exponent	Temp.Sensitivity σp-10^{-4} x k^{-1}	Flame Temp ^{o}C	Specific Impulse s	Ref.
1.	HTPB+IPDI+DOA/IPDI/DDI	5.5-6.9 (70)	-	19.9-23.7	-	-	2
2.	GAP+IPDI	10.7 (30-40)	0.44	40	1092	-	1,2,4
3.	NC + NG	6.9 (50)	0.58	34	2443	-	1,4
4.	NC + NG + DEP 50 40 10%	-			2242	235	17,20
5.	NC + NG + GAP 50 40 10%				2578	248	17,20
6.	NC + NG + DEP 37.5 50 12.5%				2284	237	17,20
7.	NC + NG + GAP 37.5 50 12.5 %				2691	253	17,20
8.	NG based CMDB propellant	6.7 (140)	0.68			252	22
9.	GAP based CMDB propellant	10.2(140)	0.55			255	22
10.	GAP+AN	2.75(70)	0.6				6
11.	GAP+PEG+AN+GN	4.5(70)	0.6				6

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