Chapter 1

Composite Solid Propellant Binders – Current Status and Advances

1.1 Introduction

All modern developments in the area of solid propulsion systems are mostly based on composite propellants. Storable propellants (solids and liquids) are usually employed for launch vehicle propulsion. The improvement in the performance characteristics is the main area of research interest in the field of solid propellants. The genesis of composite propellants which became the mainstay of today’s propulsion systems is well known. Most of the important developments in this area took place during the 19th century, which is marked in history as the first golden age of rocketry. In 1887, Alfred Nobel patented the ballistic compound based on nitrocellulose and nitroglycerine, which led to important development of new propellant formulations. Composite propellant became reality by 1940 through the pioneering work of John W. Parsons. In the early 20th century, solid propellants based on double base systems were mostly used for weaponry and liquid propellants were preferred for launch vehicle propulsion. Advantages like compactness, simplicity, reliability, long shelf life and above all lower cost per unit thrust developed make solid propellants very attractive for launch vehicle propulsion. Basically the main performance parameter used for comparison of different propellant systems is the specific impulse (Isp) which is the thrust generated per unit mass of propellant burned. Maximizing Isp is one of the main areas of interest in propellant research. In this chapter, a brief account of various propellant systems, binder systems and other ingredients that are used mainly for solid propellant applications is given.
PART I

1.2 A brief survey of development of solid propellants

Solid propellant rockets were first reported to be used by the Chinese in AD 1231 for military purpose. Development of explosives and propellants began with the use of gun powder. Detailed accounts of rockets used as weapons for war in India by the Mughals, Marathas and the legendary Tippu sultan of Mysore are documented. Reliable propellant systems with nitrocellulose and nitroglycerine based double base propellants were developed and put to use by 1939. By 1940, cast composite propellant was invented and ammonium perchlorate (AP) was used as oxidiser, which resulted in improvement of performance of the propellant systems. Many of the problems like brittleness, cracking, and high pressure index of burning associated with double base propellants could be solved by using composite propellant system. Work in the field of solid propellants started in India by mid sixties with the launching of sounding rockets with international participation and in 1978, an indigenous all stage solid propellant based launch vehicle was tested. Today, tremendous amount of research work has been carried out in this field with the support of thermochemical models and simulation using advanced computing facilities. This has been made possible due to the availability of data on thermodynamic functions of large number of chemical species. A multitude of scientific and technical expertise have been pooled to study, develop and build solid rocket motors to make solid propellant systems efficient, robust and reliable. A schematic showing the different categories of energetic materials and evolution of modern solid propellants are shown in figure 1.1. Modern propellant systems used can be categorised mainly into six different groups and the classifications are as follows.
1.2.1 Single Base Propellants

Single base propellants are in the form of powder or extruded grains, used mainly as gun propellant. These are made by gelatinising soluble nitrocellulose (NC) with nitrogen content of 12.6% in an ether-alcohol mixture, using incorporators. After adding diphenylamine, the dough is extruded through dies of required size and shape and then chopped and dried. As the name implies the system do not contain any plasticiser. The horney structure of the propellant leads to poor mechanical strength and unreliable ballistics.

![Figure1.1 Evolution of modern solid propellant](image)
1.2.2 Double Base Propellants (DB)

Double base propellants contain two bases namely, nitrocellulose (NC) and nitroglycerine (NG), which are capable of combustion in the absence of other materials. The propellant is a colloid of the two ingredients. The solubility and extent of plasticisation will depend on nitrogen content. The propellant is prepared by kneading NC and NG with stabilizers, ballistic modifiers and platonising agents etc and then carpet rolling at elevated temperatures. Finally, the mix is extruded through dies. The cast double base propellants also use same ingredients as mentioned above. The process involves mixing and casting of NC and NG with inert solvents into rocket motor case with all other ingredients. The gelling process is done at 60°C. The propellants made by this means show low elongation and high modulus especially at lower temperature and such grains are used in the free-standing configuration.

1.2.3 Triple base propellants

Triple base propellant contains a third energetic ingredient, namely nitroguanidine (NQ) also known as picrite, to the extent of 40% by weight along with NC and NG. Nitroguanidine is an aliphatic nitramine with characteristic >N-NO\textsubscript{2} group. Homogenisation of NQ in the colloidal propellant is difficult due to poor solubility. Ultra fine grade NQ can be used for complete homogenisation in the propellant. Triple base propellants exhibit good mechanical properties and good ballistic stability. Triple base propellant formulations produce less smoke and show low flame temperature. It is prepared by solvent extrusion technique.

1.2.4 Composite Modified Cast Double Base Propellants (CMDB)

The deficiencies such as lower energetics seen in double base propellants are solved to some extent by incorporating energetic solids like ammonium perchlorate and aluminium in the formulation. Reduction of the condensed species in the rocket
exhaust leading to smokeless exhaust could be achieved by introducing nitramine based ingredients like HMX in the propellant. Adding NG in the casting powder also improves processability and energetics of the propellant system.

1.2.5 Elastomeric modified cast double base propellants (EMDB)

Modification of the mechanical and interfacial properties of double base propellants is achieved by incorporating elastomeric constituents like functionalised polyesters, polybutadienes or polycaprolactones in the formulation. Except for the introduction of elastomeric additives, the methodology of preparation of EMDB is same as that of DB propellant.

1.2.6 Composite Propellants

As the name implies, they are heterogeneous systems containing a functionalised polymeric binder and a high concentration of oxidiser along with a metallic additive. The binder forms a matrix, which is impregnated/reinforced with solid additives and chemically crosslinked with curing agent. All over the world, the large solid rocket boosters use composite propellant due to the many advantages like high energetics, good mechanical and interfacial properties, processability, low cost per unit thrust, reliability and feasibility for safe handling. The larger solid propellant rocket boosters in the world utilise hydroxyl terminated polybutadiene or polybutadiene-acrylic acid-acrylonitrile terpolymer as the binder, ammonium perchlorate as oxidiser and aluminium powder as metallic fuel. Composite propellants are ideally suited for the large booster stages of satellite launch vehicles, which demand high thrust output during lift off. The main disadvantages of AP based composite propellant are smoky exhaust and pollution problems. Table 1.1 shows the largest sold rocket boosters used by different launch vehicle systems.
Table 1.1 Worlds largest solid rocket boosters using composite propellant system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>S 139 India</th>
<th>S 200 India</th>
<th>M14 Japan</th>
<th>P 230 Europe</th>
<th>ASRM USA</th>
<th>SRMU USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (M)</td>
<td>2.8</td>
<td>3.2</td>
<td>2.5</td>
<td>3.0</td>
<td>3.8</td>
<td>3.1</td>
</tr>
<tr>
<td>Length (M)</td>
<td>20</td>
<td>22</td>
<td>14</td>
<td>27</td>
<td>46</td>
<td>34</td>
</tr>
<tr>
<td>Propellant weight (T)</td>
<td>139</td>
<td>200</td>
<td>70</td>
<td>237</td>
<td>547</td>
<td>313</td>
</tr>
<tr>
<td>Propellant system</td>
<td>HTPB/AP</td>
<td>HTPB/AP</td>
<td>HTPB/AP</td>
<td>HTPB/AP</td>
<td>HTPB/AP</td>
<td>HTPB/AP</td>
</tr>
<tr>
<td>Isp-vacuum (s)</td>
<td>270</td>
<td>270</td>
<td>276</td>
<td>271</td>
<td>270</td>
<td>286</td>
</tr>
<tr>
<td>Number of segments</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

1.3 Development of composite propellants

The composite propellant was invented in 1942 at Guggenheim aeronautical laboratory, California Institute of Technology. Asphalt based propellants were the initial field study using potassium perchlorate as oxidiser. Soon ammonium perchlorate replaced KClO₄ as oxidiser which resulted in improved performance. Polysulfide binder system was used by 1950, which improved the reproducibility and mechanical characteristics. Propellants based on binder systems like polystyrene-polyester, PVC and polysulfide were developed during this period. The high modulus and low elongation of the system was not quite suitable for larger propellant grains in case bonded configuration. Hence, there was the need to develop cross linkable binder systems, which can provide suitable mechanical characteristics for the propellant over wide temperature ranges.

Introduction of aluminium as the metallic fuel was another major breakthrough in the field of composite propellants. Apart from the remarkable improvement in specific impulse, addition of aluminium also helped to suppress acoustic oscillation related combustion instability problems.¹¹ A search for more
energetic metallic additives ensued, which lead to a comparative study of various possible candidate metallic fuels like beryllium, boron, and magnesium.

Processability aspects of composite propellants were another field of thorough investigation due to the large scale processing requirement for heavier solid propellant booster stages. Solid propellant slurry containing large amount of solid additives could be handled with considerable ease due to the contemporary developments in the field of polymer rheology. The relationship between particle size, shape, viscosity of slurry and mechanical properties could be modeled to predict optimum process parameters. The models for kinetics of polymer network build up developed by Paul. J. Florry was of great help in the study of composite propellant processing.

1.4 Constituents of composite solid propellants

In general, composite propellants used in case bonded configurations are based on functionalised thermosetting binder. The binder provides a matrix to incorporate solid oxidiser, metallic fuel and other ingredients like plasticiser, burn rate modifier and antioxidants etc. Compatibility of the systems in terms of chemical, physical and interfacial characteristics is of prime importance. The different ingredients added to the system modify or introduce characteristics which together make the system fit for end use. The different additives and their respective functions are detailed in table 1.2.

1.4.1 Oxidiser

The oxidiser is the major constituent of composite solid propellant system. The oxidiser accounts for 68 to 70% by weight. Table 1.2 shows conventional and new oxidiser materials employed for propellant applications.
### Table 1.2 Oxidiser systems used for composite propellant applications

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular formulae</th>
<th>Density (g/cc)</th>
<th>Oxygen balance (%)</th>
<th>Heat of formation (kJ mol⁻¹)</th>
<th>Merits and demerits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium nitrate (AN)</td>
<td>NH₄ NO₃</td>
<td>1.73</td>
<td>19.5</td>
<td>-367.8</td>
<td>Low cost, hygroscopic nature and phase transition at 32.5°C.</td>
</tr>
<tr>
<td>Sodium nitrate (SN)</td>
<td>NaNO₃</td>
<td>2.256</td>
<td>28.2</td>
<td>-446.0</td>
<td>Naturally available. Smoky combustion products</td>
</tr>
<tr>
<td>Potassium nitrate (KN)</td>
<td>KNO₃</td>
<td>2.109</td>
<td>39.5</td>
<td>-497.1</td>
<td>Naturally available. Smoky combustion products and difficult to ignite.</td>
</tr>
<tr>
<td>Ammonium perchlorate (AP)</td>
<td>NH₄ClO₄</td>
<td>1.949</td>
<td>34.0</td>
<td>-289.1</td>
<td>Widely used. Large amount of HCl and smoke in the exhaust.</td>
</tr>
<tr>
<td>Potassium perchlorate (KP)</td>
<td>KClO₄</td>
<td>2.519</td>
<td>46.2</td>
<td>-415.0</td>
<td>High burning rate. Solid particles in the exhaust and difficult to ignite.</td>
</tr>
<tr>
<td>Lithium perchlorate (LP)</td>
<td>LiClO₄</td>
<td>2.428</td>
<td>60.1</td>
<td>-444.0</td>
<td>Highly hygroscopic and costly.</td>
</tr>
<tr>
<td>Hydrazinium perchlorate (HP)</td>
<td>N₂H₅ClO₄</td>
<td>1.940</td>
<td>--</td>
<td>-293.3</td>
<td>Highly hygroscopic and incompatible with common binders.</td>
</tr>
<tr>
<td>Nitronium perchlorate (NP)</td>
<td>NO₂ClO₄</td>
<td>2.220</td>
<td>66.2</td>
<td>+37.1</td>
<td>Highly hygroscopic and incompatible with common binders.</td>
</tr>
</tbody>
</table>

Apart from the energetics, the oxidiser has got major influence on other propellant properties. Primarily, the requirement of oxidiser is that it should easily decompose as and when required to produce necessary oxidising elements to maximise the energy release from the reaction. The oxidiser should have high...
oxygen content, high heat of formation, high density, good thermal stability, low hygroscopicity, low cost and should not undergo phase transition. Compatibility with other ingredients is another important requirement. Among various candidate materials, ammonium perchlorate is the most commonly used oxidiser. It meets many of the important requirements satisfactorily. Detailed account of mechanism of decomposition and combustion of AP is available in literature. The oxidiser also acts as reinforcement and strongly influences the rheological, viscoelastic, mechanical and interfacial properties of the propellant. The particle size distribution and shape of the oxidiser require effective control, as it affects the processing and performance characteristics of the propellant. The packing of the oxidiser crystals and adhesion to the binder play vital role in the rheological characteristics of the propellant. A major disadvantage of AP based propellant is the large quantity of HCl produced in the exhaust. Requirement of more environmentally safer system leads to evaluation of ammonium nitrate (AN). However, the phase transitions associated with AN is a major problem. Phase stabilised AN is found to be a solution for this problem. Other energetic perchlorates investigated include NOClO₄, NO₂ClO₄, N₂H₅ClO₄, N₂H₆(ClO₄)₂ and NH₃OHClO₄. The requirement of improved performance of solid propellants, environmental and safety considerations prompted synthesis and evaluation of more energetic oxidiser systems. Attempts were made to use nitramine compounds like HMX and RDX along with AP to reduce HCl emission. Realisation of a safe propellant system with specific impulse exceeding 300 seconds and density 2 g/cc along with environmentally benign characteristics is considered to be the dream of the propellant scientist. Hydrazinium nitroformate (HNF), ammonium dinitramide (ADN), hexanitrohexazaisowurzitane (CL-20), octanitrocubane (ONC) and trinitroazetidine (TNAZ) are considered energetic oxidiser systems, which could help achieve the higher performance characteristics. The structure and important performance characteristics of advanced energetic oxidiser systems are given in table 1.3. Among the prospective high energy oxidisers,
ADN and HNF are found to have positive oxygen balance. CL-20 has got great advantage in terms of high density and it is one of the most powerful explosives with caged nitramine structure.\textsuperscript{17, 18}

Table 1.3 Structure and properties of important high energy oxidizers

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical structure</th>
<th>Heat of formation (kJ mol\textsuperscript{-1})</th>
<th>Oxygen balance (%)</th>
<th>Density (g/cc)</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN</td>
<td>NH\textsubscript{4}N(NO\textsubscript{2})\textsubscript{2}</td>
<td>-150.6</td>
<td>25.8</td>
<td>1.82</td>
<td>92</td>
</tr>
<tr>
<td>HNF</td>
<td>N\textsubscript{2}H\textsubscript{2}C(NO\textsubscript{2})\textsubscript{3}</td>
<td>-72</td>
<td>13.1</td>
<td>1.87</td>
<td>122</td>
</tr>
<tr>
<td>CL-20</td>
<td><img src="image" alt="CL-20 structure" /></td>
<td>381.2</td>
<td>-10.9</td>
<td>2.05</td>
<td>167</td>
</tr>
<tr>
<td>TNAZ</td>
<td><img src="image" alt="TNAZ structure" /></td>
<td>33.64</td>
<td>-16.6</td>
<td>1.84</td>
<td>101</td>
</tr>
<tr>
<td>ONC</td>
<td><img src="image" alt="ONC structure" /></td>
<td>413.8</td>
<td>0</td>
<td>2.10</td>
<td>275</td>
</tr>
</tbody>
</table>
In octanitrocubane, all the hydrogen of cubane is replaced by nitro groups, resulting in water free combustion products. TNAZ is a stable compound with heterocyclic ring. ADN was first synthesised in Russia at Zelinsky institute. Different synthetic routes were invented and patented for organic and inorganic dinitramides by Bottaro. J. C. et.al. ADN combines all the advantages like high density, high oxygen content and low negative heat of formation. HNF was invented in 1950’s. HNF was found to have compatibility problems with polybutadiene type binders. With the advent of energetic binders like GAP, compatibility problems have been addressed satisfactorily.

1.4.2 Polymeric binders used for composite propellants

The binder is an essential ingredient of composite solid propellants. Nearly 10 to 15% of the composite solid propellant is comprised of binders. The binder largely determines the mechanical properties of the propellant. Binders used for composite propellants are organic polymers containing mostly carbon and hydrogen. It is also a fuel, which is chemically and physically compatible with all other ingredients. The decomposition of the binder should lead to large volume of stable molecules of carbon monoxide, carbon dioxide and water vapour. The most essential requirements of an ideal solid propellant binder can be summarised as follows.

i. The binder should have reactive functional groups which can chemically bond with curing agents and form elastomeric network which can provide a compatible matrix system.

ii. The binder should be hydrocarbon type, such that it can provide stable low molecular weight combustion products.

iii. The processing requirement with respect to rheology of the system should be met by a workable viscosity of the binder.
iv. Low glass transition temperature is preferred for the binder, so that it can withstand large spectrum of stress transients in operation.

v. High heat of formation is an important requirement to maximize the energetic output.

vi. Physical and chemical compatibility of the binder with other ingredients and stability of the binder system are important attributes which lead to good ageing characteristics for the system.

The modern binder systems, which can satisfy these requirements, are discussed in latter part of this chapter. Modern crosslinkable binder systems used for solid propellant formulations are listed in table 1.4.

**Table 1.4 Modern crosslinkable binders and curatives for solid propellant systems**

<table>
<thead>
<tr>
<th>Polymer resins used as binders</th>
<th>Curatives and crosslinkers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsaturated polyester based on phthalic acid, maleic acid and propylene glycol</td>
<td>Styrene or vinyl monomers</td>
</tr>
<tr>
<td>Polysulfide (thiokols LP-3) based on dichlorodiethyl formal and sodium polysulfide</td>
<td>Paraquinonedioxime or lead dioxide</td>
</tr>
<tr>
<td>Polypropylene glycol (PPG)</td>
<td>Diisocyanate and triol</td>
</tr>
<tr>
<td>Polyester (diacid and excess diol)</td>
<td>Diisocyanate and triol</td>
</tr>
<tr>
<td>Hydroxyl terminated polybutadiene (HTPB)</td>
<td>Diisocyanate and triol</td>
</tr>
<tr>
<td>Hydroxyl terminated natural rubber (HTNR)</td>
<td>Diisocyanate and triol</td>
</tr>
<tr>
<td>Copolymer of butadiene and acrylic acid (PBA)</td>
<td>Di/Triepoxy and aziridine</td>
</tr>
<tr>
<td>Terpolymer of butadiene, acrylic acid and acrylonitrile (PBAN)</td>
<td>Di/Triepoxy and aziridine</td>
</tr>
</tbody>
</table>
1.4.3 Metallic fuels

Metallic fuels improve the energetics of the propellant by virtue of the increase in chemical energy released due to the exothermic oxidative combustion reaction. Aluminium powder is the most widely used metallic additive in composite solid propellant formulations. Aluminium content of 18 to 20% in the propellant is found to improve the specific impulse by 20%. Aluminium particles in the size range of 10 to 30 µ are used in most of the compositions. Presence of metallic element reduces water content and increases the hydrogen content in the exhaust. It also improves the density of the propellant. Presence of aluminium oxide particles helps to attenuate the undesirable acoustic oscillations of the combustion products and thereby eliminate combustion instability. Other important metallic fuel choices include magnesium, boron and beryllium.

Disadvantages like poor energetics of magnesium, difficulties in ignition and combustion of boron and toxicity associated with beryllium, made aluminium a better choice. Metallic hydrides are considered promising additives, though many difficulties are yet to be solved. Metallic wires of aluminium, silver and copper are also used to enhance burn rate of the propellant.

1.4.4 Plasticisers

The processability of the highly solid filled propellant slurry is made easy by employing plasticisers which are compatible with all ingredients. Plasticisers are high boiling, nonvolatile, low viscous, low molecular weight substances. The modification of the flow characteristics of the propellant slurry is very important for realising defect free propellant grains. Plasticisers are of different types and the most widely used ester type plasticisers are dioctyladipate, dioctylphthalate and hydrocarbon plasticisers are mineral oil and paraffin oil. To improve the energetics of the propellant, plasticisers with energetic groups like azido, difluoronitramino and
nitro have been used with azido and nitrato polymers. For double base propellant applications, non-functional GAP has been used as plasticiser.

1.4.5 Curatives

The curatives react with the functional groups of the binder and forms crosslinked polymeric network structure. The number of crosslinks in the network decides the mechanical behaviour of the polymer. Selection of the curing agent is done based on the type of functional groups of the polymer. A number of curing agents have been used for propellant application. Curing agents like toluene diisocyanate, isophorone diisocyanate etc. are widely used for polyurethane matrices.

1.4.6 Other ingredients

Propellant formulations utilise a crosslinking agent, which reacts with the curatives and helps to form three dimensional network structures. Trifunctional material like trimethylol propane is an example. The crosslinking agent has the same functional group as the binder. Burn rate modifier is another important constituent, added in relatively small concentrations to modify the ballistic properties of the propellant. The selection and quantity of burn rate catalyst shall depend on the specific burn rate profile required for the propellant. Ferric oxide, ferric acetyl acetonate, ferrocene and copper chromite are usually used in propellant formulations for this purpose. Anti-oxidants are added to propellant formulations to improve the ageing characteristics by preventing oxidative degradation. Phenyl-β-napthylamine, paracresol are some of the anti-oxidants used. Certain propellants also use catalysts like dibutyl tin dilaurate and ferric acetyl acetonate as curing aids.

1.5 Basic performance requirements for solid propellants

Conservation of mass and momentum are the fundamental principles based on which the performance relations are derived for solid propellant rocket motors.
The basic performance parameters include thrust, ideal exhaust velocity, specific impulse, burning rate, flame temperature and temperature sensitivity. The initial conditions of propellant composition, temperature, oxidizer-fuel ratio and operating pressure determine the properties of combustion products or the propulsive elements exhausted through the nozzle. The thrust \( F \) developed by the rocket is given by the following expression

\[
F = m v_e + (p_e - p_a) A_e
\]  

(1.1)

Where \( m \) is the mass flow rate through the nozzle, \( v_e \) is the exhaust velocity of combustion products, \( p_e \) is the exit pressure, \( p_a \) is the ambient pressure and \( A_e \) is the cross sectional area at nozzle exit.

The most commonly used propellant performance parameter for comparison of different propellant systems is the specific impulse \( I_{sp} \), which is defined as the thrust generated per unit mass of propellant per unit time and generally expressed in seconds. Maximising \( I_{sp} \) or Density \( \times I_{sp} \) (product of density and \( I_{sp} \)) is the prime motive of the research work in this field. The \( I_{sp} \) is related to thrust by the following relationship

\[
I_{sp} = \frac{F}{m g}
\]  

(1.2)

Where \( g \) is the gravitational constant. \( I_{sp} \) is also related to the properties and conditions of combustion products and the relationship is given by the following expression

\[
I_{sp} = \sqrt{\frac{T_c}{M^*}}
\]  

(1.3)

Where \( T_c \) is the flame temperature and \( M^* \) is the mean molar mass of combustion products.

The mean molar mass is given by \( M^* = \sum (x_i m_i) \) for \( i = 1 \) to \( n \)  

(1.4)

Where \( i \) represent the component, \( x_i \) is the mole fraction of the component and \( m_i \) is the respective molecular weight. From the relationship, it is clear that the
maximum Isp shall result when combustion temperature is highest and molecular weight of the combustion product is minimum. The heat of reaction is given by the following expression

$$\Delta H = \Sigma [\Delta H_f] \text{ of products} - \Sigma [\Delta H_f] \text{ of reactants}$$

where \(H_f\) is the heat of formation.

The favorable chemical bonds in propellants and in combustion products are listed in Table 1.5.

**Table 1.5** Favourable chemical bonds in propellants and in combustion products and associated bond energies

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Propellants Bond energy (kJ mol(^{-1}))</th>
<th>Combustion products Bond energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-S</td>
<td>112.1</td>
<td>B-O 564.8</td>
</tr>
<tr>
<td>O-O</td>
<td>140.6</td>
<td>Mg-O 502.5</td>
</tr>
<tr>
<td>Cl-O</td>
<td>154.4</td>
<td>O-H 463.6</td>
</tr>
<tr>
<td>N-N</td>
<td>158.2</td>
<td>Si-O 460.2</td>
</tr>
<tr>
<td>Cl-N</td>
<td>191.6</td>
<td>H-Cl 431.4</td>
</tr>
<tr>
<td>N-O</td>
<td>238.5</td>
<td>Al-O 431.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N-H 390.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-O 350.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-S 346.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-N 336.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al=O 862.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B=O 861.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C=O 711.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mg=O 569.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N=N 945.2</td>
</tr>
</tbody>
</table>
The heat of formation of a substance depends on the bond energies between atoms of the substance. For maximising energy release, the propellant component should consist of molecules with low bond energies and the combustion products should consist of molecules with large bond energies. Hence, elements with low atomic mass and low bond energies are preferred in the reactants. Nitrogen single bonded to sulphur, oxygen or nitrogen and oxygen single bonded to oxygen or chlorine are favourable combinations for propellant formulations. Though the combustion products are of high molar mass, combustion of carbon and hydrogen release large quantum of energy. These factors imply that hydrocarbon based fuels are suitable for energetic binder application. The energy output of hydrocarbons can be improved by incorporating N, NO, NO$_2$ or NO$_3$ groups in the molecule. By substituting hydrogen with energetic groups like azido, nitro, nitrato and nitramino groups in the molecules, bond energy of the substance can be reduced and during the combustion of such compounds, large amount of heat is released with the formation of nitrogen. The important hydrocarbons developed in this fashion include polyglycidyl azide (GAP), poly 3-3 bis (azidomethyl) oxetane (P-BAMO), polyglycidyl nitrate (PGN), polynitratomethyl methyl oxetane (P-NIMMO), polyazido methyl methyl oxetane (P-AMMO).

Burning rate is an important factor influencing the performance of the solid propellant. The burning surface of a propellant recedes in a direction normal to the surface. It is functionally dependant on various parameters. Some of the parameters affecting the burning rate are combustion chamber pressure, initial temperature of the propellant, combustion gas temperature and velocity of gas flow parallel to the burning surface. The empirical equation used to represent the burn rate pressure relationship is shown in the following expression.

\[ r = a p^n \]  

(1.6)

where \( r \) is the burn rate, \( p \) is the pressure, \( a \) is a constant which depends on ambient grain temperature and \( n \) is the burning rate pressure index which is
characteristic of a specific propellant formulation. Other important parameters of interest are temperature sensitivity of burning rate and pressure sensitivity of burning rate.

Apart from the energetics, solid propellant formulation and design should address the structural strength requirements. The polymeric binder matrix possesses time dependant properties arising from viscoelastic nature. From the time a propellant grain is cast, it is subjected to a large spectrum of induced stresses, until it is burned away in the performance of it’s mission. These include forces of gravity, loads arising from propellant curing and temperature variation, shock and vibration due to handling and captive flight and finally acceleration that accompany ignition, launch and flight. A successful propellant grain design is the result of comprehensive assessment of grain structural integrity in close co-ordination with ballistic performance. The propellant mechanical properties are strongly dependant on both time and temperature. The viscoelastic characteristics of propellant cause large variation in the mechanical properties due to changes in temperature during processing and curing. At lower temperature (below glass transition temperature) or at high frequencies, the polymer exhibits high young’s modulus and could break up at higher strains. The same polymer behaves like rubbery material at high temperatures or at low frequencies. The binder plays an important role in the viscoelastic behaviour of the propellant. Hence, evaluation of the time-temperature dependence and also the effect of ageing on the mechanical properties of the propellant are important requirements. The mechanical properties to be determined for carrying out structural analysis of solid propellants fall into three groups. These are (i) the properties necessary to compute the temperature and thermally induced volume changes in the propellant, (ii) mechanical properties necessary to compute body forces due to acceleration and to define relationship among stress, strain and temperature and (iii) failure properties necessary to characterise the conditions at which failure will occur and to evaluate susceptibility to failure. The simplest form
of viscoelastic behaviour is the linear behaviour in which the ratio of the stress strain is a function of time, which can be used to compare various systems.

Density of the propellant is another important parameter of interest. A denser propellant means more energetic material mass loading in the same chamber volume. The product of density and specific impulse (density specific impulse) comprises the most important parameter for comparison of propellant systems for launch vehicle applications. The main advantage of solid propellants lies in the higher density specific impulse compared to that of other propellant systems.

From the discussion, it is clear that the performance parameters of solid propellants that are to be taken into account are of varied types. These parameters are influenced by the ingredients used in the propellant. The binder used in the propellant plays a vital role in this respect. The polymeric binder systems currently used for solid propellants for operational launch vehicles satisfy these requirements to some extent. In order to improve performance, a solid propellant with Isp greater than 300 seconds and density greater than 1.8 g/cc could be considered as a target level of performance parameters. Development of safe (hazard free) and reliable propellant systems which can meet this requirement calls for use of ingredients which are more energetic. New energetic binders which can be used in advanced solid propellant systems incorporate azido, nitrato, and nitramino groups in the molecular structure. Examples are GAP, P-BAMO, PGN, P-NIMMO, P-AMMO etc.

1.6 Composite solid propellant binders- Present status

Different types of polymeric resins were studied and employed for composite solid propellant applications in the past. The present day binder systems evolved through endeavors spread over many decades. Today, polymeric binder based composite propellants have become the mainstay of large solid rocket boosters all over the world. In this section, a brief description of various polymeric binders used for composite propellants is presented.
### 1.6.1 Polysulfide binders

Polysulfides were the first liquid functional prepolymers to be used to evaluate semi-elastic binders crosslinked by chemical condensation with a multifunctional agent. Polysulfides were first prepared by Joseph C Patrick by the condensation of ethylene dichloride with sodium polysulfide. The first case bonded propellant system was made using polysulfide based liner and propellant creating a pathway for the production of large solid rocket motors. A detailed account of the chemistry of polysulfide curing and propellant formulation is available in the literature.\(^3\)\(^4\) Low Isp of polysulfide based propellant was a major disadvantage which lead to search for better systems. Chemical structure of polysulfide binder is shown below.

\[
\text{HS} \left[ \text{CH}_2\text{-CH}_2\text{-O}\text{-CH}_2\text{-O}\text{-CH}_2\text{-S-S-CH}_2\text{-O}\text{-CH}_2\text{-O}\cdot \text{SH} \right]
\]

### 1.6.2 Polyester polyols

Polyesters like ISRO polyol with a molecular weight of 2000 is one of the resins used in this category. It is synthesised by the self condensation of 12-hydroxy stearic acid, followed by condensation with trimethylol propane.

Polyester propellants also suffer from lower Isp compared to polybutadiene and polyurethane propellant systems. Higher viscosity of the resin was also a disadvantage in this respect.
1.6.3 Polyethers

Mainly three different types of polyethers are used. Polyoxypropylene glycol (PPG) is the most commonly used resin. Lower viscosity of resin, higher energetic output and low cost are the main advantages of polyethers. Pick up of moisture on storage and gas evolution during curing reaction are the main disadvantages. Chemical structure of polypropylene glycol is shown below.

\[
\text{H-O-CH}_2-\text{-CH-OH}
\]

\[
\text{CH}_3
\]

1.6.4 Polybutadiene binders

The polybutadiene binders are originally the result of research work carried out at Thiokol nearly 60 years ago.\(^{35}\) Polybutadiene-acrylic acid (PBAA) is the first of this kind to be used. It is a copolymer of butadiene and acrylic acid. It is prepared by emulsion polymerisation, initiated by free radical mechanism using quaternary ammonium salts as emulsifier and azo bis (isobutyronitrile) as the initiator. The ratio of the monomers can be varied to meet specific polymer structural requirements and in general, there is an average of two carboxyl groups per molecule.

Polybutadiene acrylic acid acrylonitrile (PBAN) was synthesised by using acrylonitrile as a copolymer in the above system. In PBAN, there is an average of 6\% by weight of cyano groups in the polymer. Substitution of PBAA with PBAN resulted in increased tear resistance for the propellant. Chemical structure of PBAN is shown below.

\[
\text{R} \left[ \text{CH}_2-\text{CH=CH-CH}_2 \right]_n \left[ \text{CH}_2-\text{CH} \right]_x \left[ \text{CH}_2-\text{CH} \right]_y \right] \text{R} \text{COOH} \text{CN}
\]

PBAN is used in large quantities today for heavy solid rocket boosters like the systems used for space shuttle boosters by NASA.\(^{36}\) PBAN has low viscosity and
low cost of production. A combination of polyaziridines and polyepoxides are used as curing agents.

Carboxyl terminated polybutadiene polymer (CTPB) was developed in order to achieve greater flexibility for the polymer network. CTPB showed higher mechanical strength, which helped to make case bonded grain configuration with mass fractions as high as 0.94. CTPB is made by free radical polymerisation of butadiene gas using azocarboxyl initiator like azo bis (cyanopentanoic) acid. Nearly difunctional polymer with molecular weight in the range of 3500-5000 could be developed. CTPB uses aziridines and epoxides for curing reactions. A major disadvantage of aziridine and epoxide curing system is the possibility of side reactions at different temperatures and related uncertainty in the property of polymer network on ageing. The chemical structure of CTPB is shown below.

\[
\text{HOOC}[R\text{-CH}_2\text{-CH}=\text{CH}\text{-CH}_2]_n\text{R-COOH}
\]

Hydroxyl terminated polybutadiene (HTPB) combines high specific impulse with clean stoichiometric urethane reaction yielding propellant with good mechanical properties. HTPB can be produced by free radical polymerisation of butadiene gas as well as ionic polymerisation. Usually free radical polymerisation is followed. In the free radical solution polymerisation, 1,3-butadiene gas is used as the monomer. Chemical structure of HTPB is shown below.

\[
\text{HO}[\text{CH}_2\text{-CH=CH}_2]_n\text{OH}
\]

Hydrogen peroxide is used as initiator and isopropyl alcohol is used as the solvent. The polymerisation reaction is carried out at specified temperature and pressure as this step strongly influences the properties of the polymer. Other parameters include ratio of monomer to initiator concentration and solvent to non-solvent ratio. The polymer formed is precipitated in methanol and is washed and
The polymer has unsaturation in the backbone and therefore, it is susceptible to oxidation. Hence an anti-oxidant like butylated hydroxy toluene is added in small quantities.

The anionic polymer is made by living polymerisation technique using organo lithium initiator. The living polymer end is converted to hydroxyl groups by reaction with ethylene oxide. Anionic HTPB is found to have narrow molecular weight and functionality distribution. Ionic polymerisation also leads to different microstructure for the polymer. Microstructure is the arrangement of the backbone around the double bond formed during the course of polymerisation. In this case, the different microstructure results due to the arrangement of butadiene backbone around the double bond formed during polymerisation either by 1, 2 or 1, 4 addition. The microstructure of the binder plays an important role on the processability and mechanical properties of the propellant. The microstructure shows up in the form of cis, trans and vinyl forms. The various arrangements around the double bond are depicted below.

Low viscosity, higher hydrocarbon content of 98.6% (CTPB and PBAN are 97% and 92%), good reproducibility and easy availability are advantages which make HTPB the most versatile propellant binder available today. Low viscosity of HTPB helps to have solid loading up to 89% in the propellant formulation. Clean stoichiometry of curing reaction is another important advantage of HTPB. Free radical HTPB exhibits functionality close to 2.3 and requires 75 to 80 equivalence of curatives per 100 equivalence of hydroxyl groups to achieve the required properties. In the case of PBAN and CTPB, 140 equivalence of epoxy-aziridine curatives
combination is required for 100 equivalence of carboxyl groups for curing. Side reactions are also found to occur in the case of epoxy-aziridine reactions leading to requirement of higher equivalence of curatives. Due to the clean stoichiometric curing reaction of HTPB, the optimum curing is achieved in less time compared to other binder systems. HTPB can be crosslinked at relatively lower temperature (50°C) compared to PBAN or CTPB (60 to 75°C). HTPB propellant exhibits low glass transition temperature and good ageing characteristics over long periods of storage. All such superior characteristics make HTPB the workhorse binder for composite propellant application. Table 1.6 shows comparison of different binder systems.

Table 1.6 Physical and chemical properties of different binders

<table>
<thead>
<tr>
<th>Property</th>
<th>PBAA</th>
<th>PBAN</th>
<th>CTPB</th>
<th>HTPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of combustion (kJ mol⁻¹)</td>
<td>43</td>
<td>41.8</td>
<td>42.6</td>
<td>41.8</td>
</tr>
<tr>
<td>Average mol. wt. (Mn)</td>
<td>2500-4000</td>
<td>3500</td>
<td>3500-5000</td>
<td>2500</td>
</tr>
<tr>
<td>Average functionality</td>
<td>2</td>
<td>1.9</td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td>Viscosity at 25°C (poise)</td>
<td>275-325</td>
<td>300-500</td>
<td>180-350</td>
<td>40-60</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.9-0.92</td>
<td>0.93</td>
<td>0.92</td>
<td>0.92</td>
</tr>
</tbody>
</table>

HTPB-isocyanate curing reaction leads to urethane structure, which contributes to good mechanical characteristics for the propellant. Stable and reproducible propellant properties could be achieved for HTPB binder based systems. The ester linkages formed by carboxyl groups of PBAN and CTPB are comparatively inferior in this respect. Pot life, which is the processing time available for the propellant slurry after curative addition is an important parameter for propellant processing for case bonded configuration. For realising defect free
propellant grains, the propellant slurry should have a pot life of minimum 4 to 5 hours.

The cohesive strength and structural integrity of propellant depends primarily on the mechanical behaviour of the crosslinked binder, which is related to the crosslink density of the polymer network. The crosslink density is controlled by varying the content of trifunctional crosslinker and NCO/OH ratio in the formulation.

1.7 Energetic binders for composite solid propellants

Increased performance requirements, environmental impact, hazards, costs, life cycles and dual use became guiding factors in the direction of propellant development. Research in the field of energetic materials lead to development of new formulations of propellants. Large scale emission of HCl is a major problem for AP based propellant systems. Replacement of AP with energetic oxidizer systems requires use of compatible energetic binder systems to fully accomplish the advantages in terms of energetics.

Organic azides are a unique class of energetic compounds. Over the last three decades a lot of research works have been carried out to investigate different polymeric binders substituted with energetic groups like azides. The unsaturation in the inert binder systems like HTPB leads to incompatibility with energetic oxidisers like HNF. In this context, development of binder systems, which are energetic, stable, compatible and hazard free, became imperative. Substitution of energetic groups into polymers poses number of difficulties. Introduction of polar groups affects the low temperature properties like glass transition temperature. Processing and handling problems associated with sensitive systems, hygroscopic nature, ageing characteristics and above all cost were issues that had to be addressed. Substituent groups in the polymer are found to affect the physical, chemical, mechanical, rheological properties and influence the thermal decomposition in a substantial way.
Double base and AP based composite propellants with azido and nitrato substituted polymer binders have shown promising results. Azido compounds liberate about 685 kJ per azide unit during decomposition. Clean burning propellants based on AN/RDX/HMX in combination with energetic binders and oxidisers have shown potential to improve Isp above 300 seconds. By introducing cage like structure containing sufficient quantities of nitrogen, oxygen or fluorine in the formulation, energetic content and density of the propellant can be improved.

After GAP was introduced and investigated, a number of polyazido oxetanes were studied. These include polyBAMO, polyAMMO, polyNIMMO and nitrato polymers like PGN. Nitrated HTPB was another development in this area. Table 1.7 shows structure of different high energy binders developed and studied.

**Table 1.7 Chemical structure of high energy binders**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAP</td>
<td>(\text{HO}\left[\text{CH}_2\text{C}-\text{CH}_2\text{O}\right]_n\text{H})</td>
</tr>
<tr>
<td>PolyBAMO</td>
<td>(\text{HO}\left[\text{CH}_2\text{N}_3\text{C}-\text{CH}_2\text{O}\right]_n\text{H})</td>
</tr>
<tr>
<td>PolyAMMO</td>
<td>(\text{HO}\left[\text{CH}_2\text{N}_3\text{C}-\text{CH}_2\text{O}\right]_n\text{H})</td>
</tr>
<tr>
<td>PolyNIMMO</td>
<td>(\text{HO}\left[\text{CH}_2\text{ONO}_2\text{C}-\text{CH}_2\text{O}\right]_n\text{H})</td>
</tr>
<tr>
<td>PGN</td>
<td>(\text{HO}\left[\text{CH}-\text{CH}_2\text{O}\right]_n\text{H})</td>
</tr>
</tbody>
</table>
High heat of formation is an attractive feature of azido polymers. The heat of formation of the polymer becomes positive when azide group is attached to the molecule. GAP contains as much as 40 weight percent nitrogen in the molecule. The release of nitrogen during thermal decomposition increases the gaseous content of the combustion products along with the exothermic release to the tune of 685 kJ/mol. However, lower glass transition temperature of the binder is a disadvantage. Copolymers of the energetic binders have been investigated to modify many of the properties.\textsuperscript{39} Energetic polymers with hydroxyl functional groups could use isocyanate curatives to form polyurethane structure for the propellants, and thereby matched the advantages of HTPB binder system in terms of mechanical properties. Table 1.8 shows the important properties of high energy binder systems.

<table>
<thead>
<tr>
<th>Properties</th>
<th>GAP</th>
<th>Poly-BAMO</th>
<th>Poly-NIMMO</th>
<th>PGN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Pale yellow liquid</td>
<td>White solid</td>
<td>Amber liquid</td>
<td>Amber liquid</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.26</td>
<td>1.45</td>
</tr>
<tr>
<td>Mol. weight</td>
<td>2000</td>
<td>2200</td>
<td>1700</td>
<td>4510</td>
</tr>
<tr>
<td>Viscosity (cps) at (30(^{\circ})C)</td>
<td>2000</td>
<td>--</td>
<td>1600</td>
<td>2360</td>
</tr>
<tr>
<td>Heat of formation (kJ mol(^{-1}))</td>
<td>+117</td>
<td>+ 413</td>
<td>-334.7</td>
<td>- 284.5</td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>-55</td>
<td>-45</td>
<td>-30</td>
<td>-35</td>
</tr>
</tbody>
</table>

A large number of organic azides that can find application in smokeless propellant formulation have been synthesised.\textsuperscript{40-43} These include azido polyether, azido ester, azido nitramine, azido nitro compounds, azido alkenes and azido ether.
Nitrated HTPB synthesised by nitration of HTPB combines the advantages of HTPB binder and energetic nitro groups. However, a compromise is to be made with respect to mechanical properties and low temperature properties. The nitration is to be optimized at around 10% to minimise the impact on mechanical properties. Glass transition temperature of HTPB is increased from \(-75^\circ\)C to \(-58^\circ\)C by nitration due to the loss of flexibility resulting from presence of nitro groups.

1.8 Energetic material formulations with azido compounds

GAP is a unique high energy polymeric material which contains \(\text{CH}_2\text{N}_3\) moiety at pendant positions in the polymer back bone. GAP was first reported by Vandenberg.\(^{44}\) A comparison of heat of formation of ethanol (-278.5 kJ/mol) with 2-azido ethanol (+104 kJ/mol) demonstrates the effect of azide group. The three nitrogen atoms in the form of \(\text{N}_3\) are attached linearly by ionic and covalent bonds. The different resonance structures of nitrogen bonds in \(\text{N}_3\) group are shown below.

\[
\text{CH}_2\text{N} \equiv \text{N} \equiv \text{N} \quad \text{CH}_2\text{N} \equiv \text{N} \equiv \text{N}
\]

The initial research work on azido compounds were carried out to investigate the feasibility of utilizing 1,7-diazido-2,4,6 trinitrazahexane (DATH) as oxidizer and 1,3-diazido-2-nitrazopropane (DANP) as energetic plasticiser for advanced propellants. This paved the way for development efforts for hydroxyl terminated azido polymer in 1976.\(^{45}\) The polymer synthesis was initially carried out by polymerisation of glycidyl azide (GA) obtained by reacting epichlorohydrin with hydrazoic acid followed by cyclisation of the resulting product. Due to the low reactivity of the monomer, a two step process was later developed involving polymerisation of epichlorohydrin to polyepichlorohydrin followed by azidation of the prepolymer with sodium azide and finally converting it to GAP. Most of the operational solid propellants use AP as the oxidiser to the extent of 70%. The burning of conventional propellants contributes to serious impact on environment
such as ozone layer depletion and effect on stratosphere in general due to noxious chemicals such as HCl and reactive chlorine compounds. Azido and azido oxetane polymers could be used with energetic oxidizers like ADN, HNF and CL-20 to solve such problems. The advanced new generation propellant formulation could also lead to elimination of unburned fuel species and toxic materials in combustion products, which pollutes the environment. Since the azido binders do not have carbon-carbon double bonds in the polymer backbone, no compatibility problems were noted when used along with oxidisers like HNF.

The performance parameters of the propellant formulations with energetic polymers and advanced oxidiser systems have been theoretically predicted using computational methods. The theoretical estimation shows that considerable improvement could be achieved by utilising combination of energetic binders and oxidisers. Table 1.9 shows comparison of important performance parameters of a number of energetic binder systems with advanced oxidisers.

Table 1.9 Comparison of energetic propellant compositions

<table>
<thead>
<tr>
<th>Propellant</th>
<th>AP/Al/HTPB</th>
<th>ADN/Al/GAP</th>
<th>ADN/Al/BAMO</th>
<th>ADN/Al/NIMMO</th>
<th>HNF/Al/GAP</th>
<th>HNF/Al/BAMO</th>
<th>CL-20/Al/GAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt %)</td>
<td>68/18/14</td>
<td>64/18/18</td>
<td>58/18/24</td>
<td>66/18/16</td>
<td>66/18/16</td>
<td>66/18/16</td>
<td>72/18/10</td>
</tr>
<tr>
<td>Peak Isp (s)</td>
<td>265</td>
<td>275</td>
<td>277</td>
<td>274</td>
<td>280</td>
<td>282</td>
<td>266</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.76</td>
<td>1.79</td>
<td>1.75</td>
<td>1.79</td>
<td>1.84</td>
<td>1.84</td>
<td>2.01</td>
</tr>
<tr>
<td>Isp x Density (s g/cc)</td>
<td>466</td>
<td>492</td>
<td>485</td>
<td>490</td>
<td>514</td>
<td>518</td>
<td>535</td>
</tr>
<tr>
<td>Combustion temperature(K)</td>
<td>3485</td>
<td>3787</td>
<td>3819</td>
<td>3786</td>
<td>3985</td>
<td>3936</td>
<td>3746</td>
</tr>
<tr>
<td>Mol. wt of combustion products</td>
<td>28.0</td>
<td>28.4</td>
<td>30.9</td>
<td>29.2</td>
<td>29.3</td>
<td>28.2</td>
<td>29.3</td>
</tr>
</tbody>
</table>
The data indicates that AP/Al/HTPB system gives a maximum density specific impulse of 466 s g/cc at 86% solid loading. ADN/Al/NIMMO, ADN/Al/BAMO and HNF/Al/GAP propellants provide density specific impulse values of 490, 485 and 492 s g/cc at 84, 76 and 82% solid loading whereas HNF/Al/BAMO and HNF/Al/GAP give 518 and 514 s g/cc respectively at 84% solid loading. The maximum density specific impulse of 535 s g/cc is given by CL-20/Al/GAP system at 90% solid loading. The performance level can be further improved by properly tailoring the metallic fuel content. However, 90% solid loading posses a number of processing problems. So far no operational propellant system with these combinations is available in launch vehicle technology. Though HNF and CL-20 are found to show better performance, ADN is found to be advantageous in terms of feasibility and processing hazards.

The promising binder systems are BAMO followed by GAP. However, BAMO is to be used as a copolymer as it is in solid state. GAP is found to meet many of the requirements of an energetic propellant binder. Further improvement in Isp of GAP-ADN propellant can be achieved by incorporating metallic hydrides in the formulation. Aluminium hydride (AlH₃) is an attractive candidate for this purpose. Propellant formulation of GAP/ADN/AlH₃ with 25% AlH₃ could increase Isp by 18 seconds more than that of GAP/ADN/Al combination. However, lower density of AlH₃ lowers the density specific impulse of the system. Also AlH₃ has the inherent problem of high reactivity. Hence, stabilized form of AlH₃ (α-alane) or encapsulated AlH₃ is to be used. Table 1.10 shows the effect of AlH₃ in energetic propellant formulations.
Table 1.10 Effect of AlH₃ on specific impulse of propellant formulations

<table>
<thead>
<tr>
<th>Propellant</th>
<th>AP/Al/HTPB</th>
<th>ADN/AlH₃/GAP</th>
<th>ADN/AlH₃/GAP</th>
<th>ADN/Al/GAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt %)</td>
<td>68/18/14</td>
<td>66/20/14</td>
<td>61/25/14</td>
<td>64/18/18</td>
</tr>
<tr>
<td>Isp (s)</td>
<td>265</td>
<td>288</td>
<td>293</td>
<td>275</td>
</tr>
<tr>
<td>Density x Isp (s g/cc)</td>
<td>466</td>
<td>458</td>
<td>457</td>
<td>492</td>
</tr>
</tbody>
</table>

PART II

1.9 Synthetic routes of GAP and other polymers with energetic groups

Introduction of exothermically decomposing azido groups or oxygen rich energetic nitro and nitrato groups in pre-polymers result in realisation of formulation with superior performance characteristics with relatively lower oxidizer loading levels leading to better structural integrity. GAP was the first of this kind to be developed, followed by a series of azido oxetanes, nitrato and nitramino polymers.

1.9.1 Different routes of synthesis of GAP

1.9.1.1 Azidation of epichlorohydrin

Glycidyl azide prepared by azidation of epoxides⁴⁶ was used as starting material initially. In this route, epichlorohydrin is treated with hydrazoic acid to convert it to 1-azido-3-chloro-2-propanol. This is then cyclised with a base as per scheme 1.1.

\[
\begin{align*}
\text{CH}_2\text{-CH-CH}_2\text{Cl} & \quad \xrightarrow{HN_3} \quad \text{N}_3\text{CH}_2\text{-CH(CH}_2\text{Cl} \\
& \quad \xrightarrow{\text{CH}} \quad \text{N}_3\text{CH}_2\text{-CH-CH}_2\text{H}_2
\end{align*}
\]

Scheme 1.1 Conversion of epichlorohydrin to glycidyl azide
This route was discontinued as glycidyl azide monomer is unreactive and difficult to polymerise.

1.9.1.2 Carbo cationic route for polymerisation of epichlorohydrin

Azides exist in different forms and are considered as pseudohalogenes.45 As an alternative method, a two step procedure was found to be successful. In this epichlorohydrin is converted to polyepichlorohydrin (PECH) by cationic ring opening polymerization.47, 48 PECH is then converted to GAP by nucleophilic displacement of chloride by azide in polar aprotic medium. The polymerisation of epichlorohydrin is carried out by cationic mechanism in which different types of initiators and co-initiators are used. Polymerisation of PECH is done with Lewis acids such as BF₃O(C₂H₅)₂, SnCl₄, SbCl₅ or FeCl₃. Other initiators like water, aluminium alkyl salts and trialkyl oxonium salts like triethyl oxonium tetrafluoroborate and esters and hydrides of super acids like CF₃SO₃R or FSO₃R (R for alkyl groups) are also used for polymerisation of epoxy compounds.49, 50 Detailed discussion on the mechanism and procedure for polymerisation of epichlorohydrin and conversion to GAP by this route is presented in chapter 3.

By using triol as a reactant with the initiator, it is possible to get trifunctional PECH as shown in scheme 1.2.

\[
\text{H}_2\text{O} + \text{CH}_2\text{CH} (\text{CH}_2\text{Cl})\text{CH}_2\text{OH} \rightarrow \text{H} [\text{OCH} (\text{CH}_2\text{Cl})\text{CH}_2] \text{OC} \text{H}_2\text{CH} (\text{CH}_2\text{Cl})\text{O} \text{H}
\]

Scheme 1.2 Formation of PECH triol

The polymer formed is converted to GAP by reaction with sodium azide in aqueous or organic solvent medium.51, 52 Lithium, sodium or potassium azides in molar excess can be use for azidation reaction. Complete conversion of PECH to GAP takes place in dimethyl sulphoxide medium with sodium azide within 12 to 18
hours. The aqueous process utilises a phase transition catalyst like methyl tricapryl ammonium chloride and the reaction is reported to be completed in seven days. The conversion process of PECH to GAP is monitored by infrared spectroscopy. Detailed discussion on the mechanism of conversion of PECH to GAP is presented in chapter 3.

1.9.1.3 Direct conversion of epichlorohydrin to glycidyl azide polymer

Direct conversion of epichlorohydrin to GAP is carried out by gradually mixing ECH with sodium azide (mole ratio of 1:1) in presence of DMF and ethylene glycol. The reaction is done initially at 70°C followed by reaction at 90°C for 15 hours. This route leads to GAP with low molecular weight (~500) which could find application as energetic plasticiser.

1.9.1.4 Simultaneous degradation and azidation of PECH

Degradation and azidation of commercial rubbery PECH with sodium azide and a basic cleaving agent like sodium methoxide, in the presence of a triol using polar aprotic medium like DMSO or DMF has been reported for synthesis of GAP.

1.9.1.5 Synthesis of GAP with azido terminal groups

Azide terminated polymer has been synthesised by tosylation of hydroxy terminated polyepichlorohydrin with para-toluene sulfonyl chloride in presence of pyridine. Azidation is done by replacement of chlorine and tosyl group by azide by reaction with sodium azide in DMF medium. The reaction is as per scheme 1.3.
Scheme 1.3 Synthesis of azide terminated GAP by tosylation

Azide terminated GAP finds application as energetic plasticiser in composite propellants. Azide terminated GAP can also be prepared by nitration of PECH followed by azidation. The nitration is carried out using HNO₃-H₂SO₄ mixture which leads to nitro terminated epichlorohydrin. Azidation is carried out by reaction with NaN₃ in DMF or DMSO medium.

1.9.2 Synthesis of azido methyl oxetanes

Polymers and copolymers of oxetanes containing azido groups, such as 3-methyl-3-azido methyl oxetane (AMMO) and 3,3-bis-azido methyl oxetane (BAMO) are considered promising energetic binders like GAP. BAMO is synthesised in two stages. Bis (chloromethyl) oxetane (BCMO) is first prepared by chlorination of pentaerithritol followed by cyclisation of the trichloride. Azidation of BCMO with sodium azide is done in DMF medium at 85°C. The bis (azidomethyl) oxetane is then homopolymerised by carbo cationic ring opening polymerization using BF₃O(C₂H₅)₂ as catalyst in presence of butanediol as initiator at -5°C. Scheme 1.4 shows synthesis of polyBAMO.

Scheme 1.4 Synthesis of polyBAMO
Azidomethyl oxetane (AMMO) is synthesised by reacting NaN₃ with chloromethyl oxetane (CMMO) or the tosylate, 3-hydroxyl-3-methyl oxetane in presence of a phase transfer catalyst. Chloromethyl oxetane readily reacts with sodium azide in aqueous medium to yield AMMO. AMMO easily undergoes homopolymerisation to form polyAMMO. The reaction sequence is shown in scheme 1.5.

![Scheme 1.5 Synthesis of polyAMMO](image)

1.9.3 Nitrato polymers

Polynitrato methyl methyl oxetane (polyNIMMO) and polyglycidyl nitrate (PGN) are considered promising energetic polymers due to their favourable physical and chemical properties. NIMMO is synthesised by nitration of hydroxyl methyl methyl oxetane (HMMO). Nitration can be carried out using dinitrogen pentoxide or acetylnitrate. Higher yield of NIMMO (97 to 99%) is possible when N₂O₅ is used for synthesis. Scheme 1.6 shows the synthesis of polyNIMMO.

![Scheme 1.6 Synthesis of polyNIMMO](image)

Glycidyl nitrate monomer is synthesised by reacting PECH with KNO₃ in nitric acid medium for 4 hours at room temperature, followed by addition of sodium hydroxide. Polymerisation of glycidyl nitrate to PGN can be done using BF₃etherate and 1,4-butanediol combination as initiator in CH₂Cl₂ medium at 20°C for 6 hours. The polymerisation proceeds by activated monomer mechanism. The reaction is shown in scheme 1.7.
1.9.4 Energetic azido copolymers

Block copolymers of BAMO with other cyclic ethers have been synthesised for use as energetic binders with high molar mass, low polydispersity index, low glass transition temperature (Tg) and good energetics. THF-BAMO copolymers have been prepared by using trifluoro anhydride \((\text{CF}_3\text{SO}_2)_2\text{O}\) as a bifunctional initiator.\(^{59}\) Copolymer of THF and BAMO with a 50:50 ratio is a liquid polyol with Tg of -60\(^0\)C, molecular weight \(\sim 7000\) and functionality 1.9.

Triblock copolymers of BAMO, AMMO and bis (ethoxy methyl) oxetane with BAMO-AMMO block in the centre have been reported.\(^{60}\) 1,4-butanediol and BF\(_3\)etherate (1:2 ratio) is used as initiator for the copolymerisation. The reaction is carried out at -10\(^0\)C by adding a solution of the first monomer to the catalyst slowly. When 95% conversion is over, the second monomer is added. Synthesis of BAMO and nitrato methyl oxetane (NIMMO) block copolymers has been reported. 1,4-butanediol and BF\(_3\)etherate initiator is used for the polymerisation\(^{61}\) with methylene chloride as reaction medium.

New energetic copolymers based on BAMO-GAP, GAP-PGN and BAMO-AMMO has been reported. GAP-ethylene oxide (EO) polymer has also been prepared by copolymerising ECH with EO. Similarly GAP-THF based copolymers have been synthesised. BAMO-GAP based copolymer is found to have moderately high density, high heat of formation and high burning rate.
1.9.5 Azido polyesters and polyallyl azide

Energetic polyesters with functionality close to 2 are prepared from 2,3-dibromosuccinic acid and 1,2-propanediol or 3-chloropropanediol and succinic/malonic acid. These halogenated polyesters are reacted with sodium azide for conversion to azido polyesters. These polymers could be crosslinked by TDI. Polyallyl azide is synthesised by azidation of polyallyl chloride. Polyallyl chloride with molecular weight in the range of 2000 is obtained through cationic polymerisation using Lewis acid catalyst like TiCl₄/FeCl₃/AlCl₃ and aluminium powder. The polymer obtained through this route is found to be branched. The azidation of polyallyl chloride is carried out using sodium azide in DMSO medium at 100°C for 12 hours and the conversion is monitored by IR spectroscopy.

1.10 Studies on azido polymer propellants

Thermal decomposition studies of azide polymers show that heating rates and pressure do not significantly change the products of azide decomposition and decomposition of azide moiety occurs prior to that of polymer backbone. In the case of PolyBAMO simultaneous decomposition was reported. Combustion of the propellant is strongly influenced by the decomposition of polymer binder. Though azide polymers contain relatively small amount of oxygen, the heat release is due to the decomposition of the azide. Azido copolymers based on BAMO/NIMMO/polyester (PE) and GAP/THF are reported to improve the low temperature mechanical properties of propellant significantly. Theoretical estimations showed that, GAP/AP propellant could deliver a specific impulse of 2 seconds higher than that of HTPB/AP preopellant. Studies reported on the burning characteristics showed that trimethylol ethane trinitrate (TMETN) and triamino guanidine nitrate (TAGN) are very effective in increasing the burning rate of GAP/AN propellant. Komai et.al reported that a burn rate of the order of 40 mm/s at 100 ksc could be achieved for GAP/AP propellant by increasing the fine AP content. Zhao et.al
reported that the exothermic peak temperature of AN is closely related to the burning rate of GAP/mixed nitrate ester (NG, BTTN)/AN propellant and the exothermic temperature may serve as an effective burning rate modifier for GAP/MNE/AN propellant. A physico-chemical model for GAP/RDX pseudo propellant presented by Liau et.al\textsuperscript{73} showed reasonably good agreement between prediction and measured burning rate characteristics under atmospheric pressures. Studies on GAP based propellants for ram rocket application were reported by Panda et.al\textsuperscript{74, 75}

1.11 Conclusions and scope of study

This chapter brings out a brief account of importance and development of solid propellant systems. Different categories of propellants, different ingredients used and their functions in composite propellants are discussed. The importance of new generation oxidisers, binders and their advantages are discussed and compared. Synthetic routes of energetic polymers are discussed. GAP, polyBAMO, polyNIMMO and PGN are found to be promising as energetic binders. Based on the comparison of important attributes with respect to physical, chemical and energetic characteristics, GAP is found to be a strong candidate material for application as energetic binder for composite propellant applications.

Various synthetic routes for GAP and experimental techniques required for characterisation of GAP are to be surveyed and a suitable method for synthesis is to be selected. Study of the mechanism of polymerisation of epichlorohydrin (ECH) to PECH and conversion of PECH to GAP by azidation reaction are planned. It is aimed to synthesise PECH by different routes and to do a parametric study of the polymerisation followed by detailed characterisation. Process parameters that control the properties are to be identified and evaluation of kinetics of conversion of PECH to GAP is envisaged. It is also aimed to scale up the polymerisation process of ECH and synthesis of GAP.
The investigation encompasses a detailed mechanical, morphological and structure property study of GAP. Detailed thermal analysis to study the kinetics of thermal decomposition of GAP and compounds of GAP. Detailed studies on the glass transition characteristics and phase morphology of GAP and GAP-HTPB blends are also planned for this investigation by calorimetry (DSC) and dynamic mechanical analysis (DMA).

We have undertaken a comprehensive evaluation of the performance parameters to study the suitability of GAP based propellant formulations. It is planned to find a correlation between viscosity build up and curing reaction of GAP from kinetic data generated by viscometry and FTIR spectroscopy studies. It is also planned to investigate the effect of different plasticisers on GAP. Evaluation of GAP based propellant formulations for mechanical, ballistic and rheological properties is also envisaged.

1.12 References


