Solid Propellant Binders

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Solid propellants are widely used in modern rockets and missiles. Although the history of solid rockets could be traced to the discovery of gunpowder over a thousand years ago, the technology could be perfected only by the later half of the 20th century. The failure of gunpowder rockets was largely due to the unknown consolidating technique of the powder composition. The emergence of large solid propellant motors had to await the dawn of polymer science and technology (S&T). Specific syntheses of functionally terminated polymers having cross-linking capability led to the emergence of casting technology of solid composite propellants. This review describes the various polymeric fuel/binder systems used or considered for use in solid propellants. It includes a brief background, advantages, and shortcomings of the various systems, an account of the currently used binders and a critical survey of the advanced polymers envisaged for future usage. Special emphasis has been laid on recently synthesized polymers having N-N bonds in their structures, and on the feasibility of developing smokeless propellants based on ammonium nitrate.

Introduction

Chemical propellants are the main source of propulsion energy of rockets and missiles. The enormous amount of energy needed to launch a space vehicle is provided by the controlled combustion of a chemical combination of a ‘fuel’ and an ‘oxidizer’, known as propellant. A rocket fuel is basically a reducing agent, which when oxidized, would release high heat energy and gaseous products. Of the various fuel/oxidizer combinations, depending on their physical states, solid composite propellants comprised a powder oxidizer embedded in a matrix of a fuel, are the ones used very widely. The solid propellant rockets are easier to handle and in ready-to-use condition all the time. Initially, the solid propellants were meant for combat rockets only, but their simplicity and availability in almost unlimited size have led them to be used as the main, sustainer or booster charge for many types of rockets and missiles. The immense progress in solid rockets may be noticed by comparing the size of the solid boosters. The first booster charge developed for JATO (Jet-Assisted Take-Off) aircraft weighed only 28.2 kg, while the giant size booster used in Space Shuttle, e.g., is a 3.7 m diam and 38.47 m long grain, having 504 t of propellant.

Historical Background

Historically the first solid rockets were projectile launchers in war, based on gunpowder (also known as black powder) comprising a mixture of potassium nitrate (oxidizer), charcoal and sulphur (fuel/binder). The compressed mixture contained in a metal tube with a hole on one end formed the crude rocket. Tippu Sultan, the king of Mysore in the late 18th century, used them profusely in his battles. In those days, military rockets were not in use in Europe, but they were in existence in India. They were borrowed by the British after having been themselves exposed to rocket attack near Seringapatam in 1799 in wars against Tippu. These were, however, crude rockets lacking range, safety and accuracy, and largely unreliable.

The gunpowder sticks (grains) made simply by compressing the charge to a reasonably high density to make it uniform, cannot be defect-free as compressing makes the grain excessively brittle. Brittle charges develop hairline cracks invisible to the eye on temperature change during storage or while transporting from one place to another. The combustion of propellants having cracks or holes is erratic, and often results in explosion.

This inherent flaw of the gunpowder rockets, however, was not understood till the later part of the 19th century. It is thus obvious that large size rocket grains could not be made by the charge compression technique.

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The next important step in combat rockets was the introduction of smokeless powder comprising nitrocellulose (NC) and nitroglycerine (NG) by A Nobel in 1890. The so-called, ‘double base’ (two explosive components) or ‘homogeneous’ propellant was a plasticized mass of NC and NG. The propellant slurry made by using a solvent could be given a shape either by extrusion process or by casting into containers. The homogeneous propellants are essentially defect-free and, therefore, more reliable. They have been extensively used in sounding rockets and as ‘sustainer’ grains for missiles. Propellant grain sizes varying from 60 to 200 mm (outer diam) and weighing 5 to 200 kg have been developed for different applications. However, it is difficult to make very large size grains by the hydraulic extrusion process or by the gel casting technique since the propellant mass becomes porous while driving away the residual solvent.

The technology of making large size grains emerged along with the basic understanding of polymer science. The so-called composite solid propellants came into existence largely because of the significant advances made in developing polymer casting techniques soon after WW II. It was indeed a clever idea of chemists to use functionally terminated organic polymers which could be used both as high-energy fuels, and also as binders to consolidate the powder oxidizer. It was envisaged that viscous pre-polymers could be mixed with solid powder composition to form a slurry that could be cured in situ after casting in suitable moulds.

**Energetics**

The power of a propellant is often expressed in terms of specific impulse (Isp). It is defined as the impulse (thrust x time) per unit weight of propellant. The equations relating Isp with the chemical parameters are described as follows:

\[ \text{Isp} = F \times T / W; \quad \text{Isp} = (\Delta H)^{1/2} \times T / M_c \]

where, \( F \) = thrust, \( T \) = time, \( W \) = weight, \( \Delta H \) = heat release (heat of combustion) per unit weight of propellant, \( T_c \) = chamber temperature, and \( M_c \) = average molecular weight of combustion products.

It is obvious that high heat of combustion and low molecular weight products are the basic requirements for achieving higher Isp. Since the heat of combustion is dependent upon the heats of formation of the propellant constituents (fuel and oxidizer), it is desirable that they have high heats of formation. Fuels and oxidizers having positive or low negative heats of formation are, therefore, preferred. Similarly, low molecular weight product species help in improving the Isp. Hydrogen for that matter is not only a good fuel but also a desired exhaust product.

**Solid Oxidizers**

Like the gunpowder, a composite propellant is a heterogeneous mixture of basically a powder inorganic oxidizer and a fuel (binder). Usually, a metal like powder aluminum and other ingredients are added to improve the performance characteristics. Since the main criteria of a propellant composition is to produce high heat of combustion and low-molecular weight gaseous products, solid oxidizers producing completely gaseous products are therefore preferred. A quick survey of the various inorganic oxidizers, centered usually around the nitrate and perchlorate salts, revealed that ammonium perchlorate (NH\(_4\)ClO\(_4\)) and ammonium nitrate (NH\(_4\)NO\(_3\)) could be the right candidates. Unlike potassium nitrate and potassium perchlorate, used in gunpowder and asphalt propellants, respectively, these oxidizers produced totally gaseous products. Besides, ammonium perchlorate (AP) had very favourable other properties, like high available oxygen, high density, non-hygroscopicity, easy storability, and low sensitivity. These characteristics have made AP the workhorse oxidizer of solid propellants. Indeed, it has been the monopoly oxidizer of virtually all the large-size solid propellant rockets, worldover for the past 50 y or so.

Ammonium nitrate (AN) also produces completely gaseous products, which are even smokeless. It is also relatively very cheap but its inherent characteristics, like low energy, hygroscopicity, an awkward phase change around room temperature and very low burning rate (discussed later) have been deterrents to its large scale use in solid propellant compositions, so far.

Other non-metallic oxidizers have also been examined but have not been found suitable for use for one reason or the other. Nitronium perchlorate (NO\(_2\)ClO\(_4\)), investigated extensively in 1970s, e.g., has a positive heat of formation and a highly favourable oxygen balance but was discarded because of its instability in the presence of moisture. Ammonium dinitramide (ADN) also has high available oxygen and a relatively low negative heat of
formation but its synthesis is hazardous and complicated, and reported to be exorbitantly costly in the US. Unconfirmed reports suggest that the Russians have used ADN in certain missiles, and a way has been found to synthesize this material cheaply. Hydrazinium salts, like the nitroformate, mono- and di-perchlorates, have also been examined, but either they have little available oxygen or are highly sensitive to explosion.

**Polymeric Binders**

After having selected ammonium perchlorate as the oxidizer of choice the emphasis of research was shifted to evolving the right type of fuels (binders). Here again the chemical composition of the fuel should be such that basically it gives high combustion energy (calorimetric value) with AP and low molecular weight products. A careful consideration of the combustion energies of the elements revealed that the only elements that produced relatively high combustion energy, and also produced gaseous products, are hydrogen and carbon. Although many light metals, like Li, Be, B, Mg and Al have higher combustion energies but they produce condensed (solid ash) products. It thus follows that the search for solid propellant fuels has to be focused primarily on compounds of hydrogen and carbon or simply stated, hydrocarbons. Further, since hydrogen has higher combustion energy per unit weight than carbon, a hydrocarbon with high H/C ratio is preferred.

A processed solid propellant grain must possess good mechanical strength. In order to provide the structural integrity to the powder oxidizer, it was felt that the fuel used should necessarily be a long chain molecule, which could form a cross-linked matrix on curing. Organic polymers, made of long chain hydrocarbons, thus became the prime contenders of propellant formulations, as they could serve the dual purpose of a high-energy fuel as well as a matrix forming binder.

The main idea behind the use of polymers in propellant formulation was to evolve a casting technology of large-size, defect-free grains. As stated earlier the idea was to mix the powder oxidizer with a viscous pre-polymer having suitable end-groups and a curing agent, to form a pourable slurry which could be cast in a container of a pre-determined size and geometry. The curing reaction (process of cross-linking) would be so chosen that the end-groups link with the curing agent without liberating any small molecules, like H₂O, CO₂, SO₂, etc., since the liberation of small molecules and/or their subsequent removal makes the grain porous and hence is undesirable. The slurry would solidify (cure) simply on raising the temperature or on standing for a while. The mix would then contain an oxidizer embedded in a matrix of polymer (fuel). Such a grain would be free of voids, and form a monolithic structure. It would also possess the desired mechanical strength because of the cross-linked polymer-matrix structure.

**Early Systems**

The history of solid composite propellants could be traced back to the pioneering work of Von Karman, Frank Malina, John Parsons and Edward Foreman at the Guggenheim Aeronautical Laboratory, California Institute of Technology (GALCIT) USA, while developing a solid fuel rocket for JATO aircraft in 1939. The charge for JATO consisted of ammonium nitrate as the oxidizer, with black powder and cornstarch as the fuel and inhibitor, and glue as the combustible binder. Another formulation, GALCIT 53, was introduced in 1942. It consisted of potassium perchlorate as the oxidizer, dispersed in melted asphalt (as both fuel and binder) and poured while hot into cylindrical moulds. When cooled down the “cured” propellant cylinders were inserted into the rocket casing. This was the first “cast” solid propellant that permitted the production of solid rockets of any size or shape. However the asphalt composites were found to have poor physical properties, such as poor tensile strength and cracking under normal temperature cycling.

Based on the experience with the asphalt compositions, it soon became evident that better physical properties could be achieved by the use of cross-linked thermosetting polymers. Polysulphide rubber as a castable fuel/binder was adapted in 1945 by Bartley at GALCIT. Propellant compositions having potassium and/or ammonium perchlorate were cast with Thiokol LP-3 polysulphide liquid polymer. This became the basis for the most modern large-scale cast solid-fuel rockets. The polymer, ethyl formal polysulphide, was prepared from dichloro-ethylformal and sodium polysulphide using a small amount of trichloropropane cross-linker. Many
variations in the polymer formulation were followed subsequently. Studies of these materials in propellant formulations carried out at JPL, Thiokol Chemical Corp. and at other propellant companies, let to a significant understanding of the chemistry of solid propellants. The presence of heavy sulphur atoms in the polysulphide rubbers, however, decreases the performance, hence these rubbers were subsequently replaced by hydrocarbon (CHNO) polymers.

By this period the chemistry of solid propellants was fairly well understood. Chemists knew the basic requirements a polymer should have in order to cast large-size high-energy grains having good mechanical properties. Several polymeric binder systems were evolved, almost simultaneously at JPL, Aerojet-General, Thiokol, and General Tire, and Rubber chemical corporations.

Unsaturated Polyesters

One of the earliest polymer systems available and considered for propellant formulation was the unsaturated polyesters. Polyester systems, in general, have higher fuel values than the polysulphides and could be manufactured to specific molecular weights and viscosity. The unsaturated polyesters are usually prepared by condensing a dicarboxylic acid with a dihydric alcohol, one or both of which contain the olefinic bonds. These bonds are utilized in cross-linking via simple vinyl monomers, like styrene and methylacrylate. The addition of the low molecular weight olefin fluidizes the propellant mix. The cross-linking process could be initiated by peroxides and controlled by the number of unsaturated sites in the polyester pre-polymer. Additional plasticizers could be used to adjust the propellant mix properties.

Several acceptable propellant formulations were developed, particularly by the Aerojet company around 1946. The grains made with styrene/polyesters had good aging characteristics, but had hard structure and could not bond to aluminum or steel walls, thus were unsuitable for case bonding. They were also smoky and not high performing. The polyester propellants have now been replaced by high performing polybutadiene compositions.

Plastisol Propellants

The plastisol propellants (also known as PVC propellants), differ from composite propellants in the technique of solidifying the mass. While in composite propellants the solidification (curing) is accomplished by cross-linking the pre-polymer using a tri- functional curative or opening-up of vinyl bonds, in plastisol propellants it is achieved through solvation (solution) of the resin powder in a non-volatile liquid, which also acts as a plasticizer for the resin.

Usually, polyvinyl chloride (PVC) powder is used as the resin and an ester like dioctyl phthalate, as a plasticizer. Finely divided PVC powder is mixed with the plasticizer in almost equal amounts. To the resulting slurry an oxidizer like AP, sufficient to oxidize both PVC and the plasticizer is added along with other ingredients, such as a metal powder and stabilizers. The mix is poured into moulds and heated to about 170 °C so that PVC dissolves into the plasticizer. The mixture on cooling to room temperature solidifies into a homogeneous mass having good tensile strength and smooth surface.

Used widely in sounding rockets and tactical missiles, the PVC propellants are not case-bondable. Heating the PVC at high temperature causes it to decompose partially splitting HCl. Modifications in composition and processing procedure of PVC propellants have been recently reported. However the plastisol process is unsuitable for making large grains.

Polyurethanes

A binder system, capable of many variations results from the reaction of difunctional alcohols (diols) with diisocyanates to form polyurethanes. The noteworthy feature of this reaction is that no small molecules are split out when the two moieties are joined together, unlike the condensation reaction. The hydroxyl terminated pre-polymer backbone may be varied; it could be a polyester, polyether or polybutadiene. Usually, toluene diisocyanate is used as chain extender for polyurethane formation. The new polymer has diisocyanate end-groups, which could be subsequently cross-like using a triol, like glycerol. Of the three types of pre-polymers the polyesters (e.g. neopentylglycolazelate) are not desirable because of their relatively high viscosity and low specific impulse (Isp) with AP oxidizer. The hydroxyl terminated polyethers, like poly(oxypropylene)glycol, are easily available, have low viscosity, and adequate rate of cure and good aging characteristics, but give lower performance.

Hydroxyl Terminated Polybutadiene (HTPB)

The HTPB polyurethane binder system gives the highest specific impulse with AP oxidizer. A
relatively late comer, HTPB is the only pre-polymer which was specifically synthesized for its use as a propellant binder. It is usually produced by the free radical solution polymerization of 1,3-butadiene using hydrogen peroxide initiator. The pre-polymer has molecular weight in the range, 2500 to 2800; average functionality, 2.2 to 2.4; and viscosity, 65 P at 30°C. Originally marketed by Atlantic Richfield Company, USA, under the trade name ARCO R-45, in India it was synthesized and developed at VSSC (ISRO), Trivandrum, and the process know-how transferred to M/s NOCIL, India, for production.

Besides HTPB the ISRO has also developed two more hydroxyl terminated binders, namely the ISRO Polyol and a hydroxyl terminated natural rubber, (HTNR). The ISRO Polyol, based on castor oil, is a saturated ester with low molecular weight (~2000), nearly bi-functional, having a viscosity of about 20 P at room temperature. The hexyl pendant groups impart good low temperature properties in addition to making it a self-plasticized system. It is cured with isocyanates and trihydroxy compounds, similar to HTPB. Copolyurethanes of HTPB and ISRO Polyol made with diisocyanates of toluene and hexamethylene have also been studied. The ISRO Polyol propellants have been used in sounding rockets.

Many favourable properties of the polyurethane system, like high density, rapid burning rate, high tensile strength, excellent fuel value, etc., makes it a binder of-choice. As a matter of fact the most widely used binder system used currently is based on HTPB polyurethane.

Polyurethane binders for solid propellants were independently developed by chemists at Aerojet in 1948, and at JPL in 1953 (ref.8). The first successful use of the propellant based on polyurethane with AP as oxidizer, was made by Aerojet for the Hawk surface-to-air missile system in 1954. It was a highly successful propellant; the Aerojet supplied over 40,000 Hawk motors to the US Army from 1954 to 1990 (ref.4). Minuteman was America’s first all solid-fuel ICBM, whose development started in 1958. The propellant used in its second stage was polyurethane/AP/aluminum powder. The HTPB-polyurethane is the most suitable and widely used binder system for large solid boosters. For example the giant Delta and Titan IV rockets, the Ariane strap-on boosters and the Japanese H-II, all use HTPB based propellants. In India the solid boosters of the satellite launch vehicles, ASLV, PSLV and GSLV are based on HTPB propellants. The main first stage of the PSLV consists of a 2.8m diam core motor having 140 t of HTPB/AP/Al propellant providing over 500 t of thrust. In addition, the Rohini series of sounding rockets ranging from RH-75 to 560-mm diam motors also contain HTPB propellants.

**Carboxyl Terminated Polybutadienes**

Carboxyl groups condense easily with epoxides and aziridines without liberating any small molecules. This reaction has been the basis of evolving pre-polymers based on carboxyl terminated polybutadiene (CTPB). Liquid polybutadiene pre-polymers and its copolymers with acrylic acid and acrylonitrile having carboxyl groups have been synthesized and used extensively in producing very large size propellant grains. Being composed of almost a pure hydrocarbon chain, polybutadienes have high calorimetric values, and are preferred fuels. As binders they provide high solid loadings and satisfactory mechanical properties to the grain over a wide range of temperatures.

Polybutadiene-acrylic acid (PBAA) was the first butadiene copolymer to be used in a rocket motor application. Owing to the method of preparation the liquid polymer is a mixture of non-functional, mono-, di- and polyfunctional segments. As a result the epoxide-cured systems show poor reproducibility of mechanical properties and therefore, PBAA Is no more used as a binder.

The terpolymer, polybutadiene-acrylic acid-acrylonitrile (PBAN) provides much better storage and mechanical characteristics to the propellant grain. The introduction of acrylonitrile moiety improves the spacing between the carboxyl species and provides better control of curing process. Since its introduction in 1957, more solid rockets were produced with PBAN than any other polymer till 1975. Since then PBAN has been largely replaced by more energetic polymers, CTPB, and HTPB. The Space Shuttle boosters are based on PBAN propellants. The first Indian Satellite Launch Vehicle (SLV-3), launched successfully in 1980, also used the PBAN/AP propellants.

Both, in PBAA and PBAN the carboxyl groups appear as pendent groups. The random location of the carboxyl groups was leading to open chain ends that were not effective in providing good physical properties. Ultimately, polybutadienes were developed with carboxyl groups in the termination position to take full advantage of the entire length of
the polymer chain. These pre-polymers marketed as Thiolok HC434 and Butarez CTL, were synthesized by a free radical or lithium initiated technique to an average molecular weight of 3500-5000, and had nearly a bi-functional structure, i.e., one carboxyl group at each end of the polymer chain. The curing (cross-linking) of CTPB is achieved by reacting with trifunctional epoxides (e.g. Epon X-801) or aziridines (e.g. MAPO). These attributes of CTPB helped in achieving substantially improved mechanical behavior of highly loaded solid propellants, particularly at low temperatures. The CTPB based propellants provide very high specific impulse, just about 1 s less than the HTPB/polyurethane system.

A pre-polymer akin to CTPB, called REF 20, has been developed by ISRO. It is a lactone-terminated polybutadiene, having a molecular weight of about 3000 and a viscosity in the range 200-300 P. It gives superior mechanical properties as compared to CTPB at the same solid loading. It was used in the upper stages of SLV-3 and ASLV rockets and as apogee kick motor to put the ‘Apple’ satellite into orbit.

Epoxy Resins

Resins having epoxy end-groups have been used as propellant binders, as they exhibit good processability, low cost, excellent case-bonding nature and good mechanical properties. Fairly high Isp could be achieved with epoxy binders. Various types of epoxy resins are available commercially the most common being the one based on bisphenol-A. The epoxides can be easily converted to thermosetting polymers by reacting with curing agents like primary or secondary amines, and dicarboxylic acids. One of the important advantages of the epoxy resins is that there is virtually no change in volume (shrinkage) after curing. Lately, diglycidylamine epoxy resins, based on bis-hydrazones having N-N-bonds in the backbone (discussed later) have been prepared specifically for their use in solid propellants.

Energetic Binders

Of the many issues relating to the rocket performance, maximizing the specific impulse (Isp) has remained the major criterion, so far. Most studies have been aimed to achieve higher Isp by opting for more energetic oxidizers and fuels (binders). Approaches to improve the energetics of the binder, involves the introduction of explosophile groups, like –NO₂, -ONO₂, -NF₂ and N₃ in the polymeric chain. These groups contribute to increase in the heat of formation (making it more positive) of the polymer, and hence enhance the overall heat of combustion. The density of the polymer is also increased which means higher amount of the oxidizer could be loaded per unit volume. The presence of an oxidizing elements in the binder could be advantageous as it reduces the amount of loading of the powder inorganic oxidizer (AP) required for complete combustion, thereby making the mixing of the ingredients easy. This is indeed beneficial from both the processing and performance aspects. For AP/CH₄ propellants the stoichiometric (oxidizer/fuel) ratio being, 90.5/9.5, it is not possible in practice to process grains having such a high oxidizer loading with adequate mechanical strength. The upper limit of loading being about 86 per cent, most AP-based propellants are fuel-rich and hence give less than the expected theoretical specific impulse.

Another approach is to introduce metal elements into the polymer backbone. Since light metals have higher heats of combustion, their introduction in the polymer itself, instead of adding as powder, (a metal powder is usually added to the propellant mix to increase the Isp) would result in enhanced energy. With this view, several polymers containing Al, Mg, and Boron in the backbone were synthesized in the 1960s.

While many of these options look attractive, there are several associated inherent problems. For instance the use of energetic binders often causes stability and compatibility problems. The energetic material containing oxygen and fluorine groups, which are introduced at the expense of hydrogen, lower the Isp to some extent. The rheological properties are also adversely affected in most cases. Moreover the introduction of both the oxidizer and fuel groups in the same molecule makes it overly sensitive and hazardous to handle. Special precautions have to be taken particularly in synthesizing such materials. Beside, there are many other considerations that have assumed greater significance in recent years. These are, cost, safety, reliability, environmental impact, transportation, long self-life, etc. Any new binder produced must prove to be better performer with respect to these aspects too.
Azide Polymers

The most prominent among the energetic polymers are the ones containing the azido groups. The hydroxyl terminated polymers of azidomethyl-oxirane (epoxide) and oxetane have been prepared for their use as binders. Of these the most widely studied is the glycidyl azide polymer (GAP) of the oxirane family. It is a un-crosslinked polyol, and is a viscous liquid at room temperature. It has an average functionality of 2.7 hydroxyl groups, and molecular weight, 700. This polymer has been prepared at various propellant research laboratories by reacting polyepichlorohydrin with sodium azide, varying in functionality as well as molecular weight. GAP is now commercially available, marketed by the Special Chemicals Division of 3M company. GAP cured with a disiocyanate by itself sustains combustion and hence has been examined as a fuel for integrated ramrockets.\(^{14}\) When used as a plasticizer, it is found to enhance the burning rate of AP/epoxide propellants.\(^{15}\) AP/GAP propellants have poor mechanical properties, especially the elongation at low temperatures.

Other promising azide polymers are the poly (bis-azidomethyl)oxetane (BAMO) and poly (azidomethylmethyloxetane (AMMO). Poly BAMO is a stiff solid, while poly AMMO is a soft elastic polymer. Copolymers of BAMO and AMMO, have been successfully synthesized at Thiokol, which are thermoplastic in nature.\(^{13}\) The thermoplastic elastomers (TPEs) having 'hard' and 'soft' segments are useful since their co-crystallization itself forms the necessary three-dimensional network of interlinked soft unsymmetrical polymer blocks. No cross-linkers are used in the solidification process.

The concept of using the TPEs, having hard and soft segments as binders is relatively new. It essentially evolved because of the immense difficulty faced in disposing the solid propellant grains, which are actually thermosetting type cross-linked composites. The only way to destroy such a mass (after its useful life) is by burning, which causes pollution if carried out in open atmosphere. Degradation of the chemical and disposing in a closed cycle reactor is very expensive and not an easy task. In fact, more efforts are being made in finding efficient ways to disposing a solid propellant grain than to produce a new one! The TPE binder systems are preferred because they can avoid this destruction process. The physical cross-links formed on co-crystallization between the hard and soft segments are reversible and disappear above the melting point of the crystalline hard block. The propellant ingredients could thus be reclaimed by simply melting the propellant grain, and subjecting them to recovery processes. It is a wonderful concept, it if works. Oxetane thermoplastic elastomers have the potential to play a major role in the next generation of propellants, explosives, and pyrotechnic systems, according to Miller\(^{13}\).

Mixed Polymer Networks

Although the HTPB-polyurethane system provides the highest specific impulse for AP-based propellants, in certain situations adjustments of the combustion and mechanical characteristics are needed depending upon the mission requirement. Mixed binder network systems, composed of two copolymers, or interpenetrating polymeric chains, have been proposed to improve these properties. Studies on AP propellants with interpenetrating polymer chains of HTPB and poly styrene or polymethylmethacrylate as binder, have proven the usefulness of this concept.\(^{16}\) It helps in fine tuning the propellant characteristics. Similarly the co-polyurethanes made of HTPB and ISRO Polyol have been examined in detail. It is noticed that by varying the ratio of the two hydroxyl pre-polymers, chain extenders, and cross-linkers, copolyurethanes having a wide range of tensile strength and elongation could be obtained.\(^{7}\) When these copolyurethanes are used as a binder, they are shown to alter the burning rate and mechanical properties of AP propellants.\(^{17}\) A detailed study pertaining to characterization and modeling of network parameters of co-polyurethanes has been carried out.\(^{18}\)

N-N-Bonded Polymers\(^{19-27}\)

Polymers having nitrogen-nitrogen (N-N) bonds in their structures are relatively new comers. The self-igniting (hypergolic) nature of N-N bonded compounds, like the hydrazines and even solid hydrazones on coming into contact with liquid oxidizers like nitric acid and nitrogen tetroxide, is well known. It was considered worthwhile to synthesize polymers having N-N bonds, initially as fuels for hypergolic hybrid rockets. For the first time, epoxy terminated hydrazones resins were prepared in the author’s laboratory at the Indian Institute of Science\(^{19-22}\). These polymers are low molecular
weight viscous resins of carbono- or thiocarbono-hydrazones having diglycidylamine epoxy end-groups. The synthesis of these resins is simple, non-hazardous and cheap. The overall attractive characteristics of these polymers led to examination of their role as binders for solid composite propellants. Several new diglycidylamine epoxy terminated dicarboxyl bis(hydrazones) were prepared\textsuperscript{23,24} subsequently, and a detailed study followed. It is interesting to note that a variety of resins could be synthesized simply by changing backbones and also the substituent groups but using the same procedure. The much desired alteration in their properties to suit specific propellants characteristics could thus be made by simply choosing the most suitable polymer. Of late the hydroxyl terminated N-N-bonded resins have also been synthesized\textsuperscript{25}.

Characterization data of some of these resins\textsuperscript{26,27}, listed in Table 1, reveal that they have adequate viscosity for high solid loading and relatively high density. A higher density of these resins means that the density specific impulse (Isp.d) of propellants could be much higher than those based on polybutadiene binders\textsuperscript{9,26}.

Table 1 — Properties of some N-N-bonded resins and CTPB

<table>
<thead>
<tr>
<th>Resin</th>
<th>Viscosity at 35 °C (poise)</th>
<th>Heat of combustion (kcal/g)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diepoxide of bisfurfuraldehydecarbonohydrazone (DEFCH)</td>
<td>404.7</td>
<td>5.74</td>
<td>1.37</td>
</tr>
<tr>
<td>Diepoxide of bisfurfuraldehydethiocarbonohydrazone (DEFTCH)</td>
<td>467.4</td>
<td>6.00</td>
<td>1.37</td>
</tr>
<tr>
<td>Diepoxide of sebacoyl bisfurfuraldehydrazone (DESFH)</td>
<td>100</td>
<td>6.45</td>
<td>1.22</td>
</tr>
<tr>
<td>Diepoxide of adipoyl bisbutanonehydrazone (DEABuH)</td>
<td>157</td>
<td>6.64</td>
<td>1.15</td>
</tr>
<tr>
<td>Diepoxide of sebacoyl bisbutanonehydrazone (DESBuH)</td>
<td>75</td>
<td>7.13</td>
<td>1.12</td>
</tr>
<tr>
<td>Carboxyl Terminated Polybutadiene (CTPB)</td>
<td>-150</td>
<td>9.70</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The main role of a binder is to provide adequate structural integrity to the propellant grain. The polybutadiene binders are much preferred because of their rubbery nature. In general the propellant grains processed with carbono- or thiocarbono-hydrazone based resins have hard structures. However, typical compression strength data\textsuperscript{26} of the AP based propellants, shown in Table 2, indicate that it could be varied considerably. Apparently the mechanical strength of the dicarboxyl hydrazone resins based systems depends upon the number of the spacer (CH\textsubscript{2}) groups in the parent molecule. Propellants processed with the resin having eight spacer groups (e.g. DESBuH) have mechanical properties quite close to those based on CTPB\textsuperscript{26,28}.

A general weakness of any propellant system concerns its burning rate. The control of BR is an important aspect of solid propellant formulations. Propellants having different BRs are needed depending on the mission requirements. Since the BR essentially depends on the chemical composition, i.e., oxidizer, fuel, and their ratio, (at a particular pressure), it is fixed once the composition is decided. The variation required is usually effected by using catalysts, although they are least desired as they adversely add to the dead weight, and also affect the
aging characteristics. The BR of AP propellants could also be enhanced to some extent by using the ultra-fine particles of AP. But making and storing of ultra-fine powder is a difficult task. Instead, altering the BR by changing the fuel (binder) is a highly desired proposition as it is used as a minor component (< 14 per cent). It thus makes sense to develop new binders when a significant increase in the BR is required. In this context, it is interesting to note that the N-N-bonded polymers when used as binders, increase the burning rate significantly (Table 3). For AP propellants, an almost three-fold increase in the burning rate over that processed with polybutadiene (CTPB) binder^{26-29} is noticed. This is significant, as increment of this magnitude in the BR is not normally possible with the hydrocarbon (CHO) binders. It is the presence of the N-N bonds in these binders which is responsible for the high combustion reactivity in these propellant systems.

Table 3—Burning rates of AN, PSAN and AP based propellant compositions

<table>
<thead>
<tr>
<th>Propellant composition</th>
<th>Burning rate at 70 atm</th>
<th>Pressure index</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN/DEFCH</td>
<td>2.78</td>
<td>0.33</td>
</tr>
<tr>
<td>PSAN (KNO₃)/DEFCH</td>
<td>4.28</td>
<td>&gt;0.8</td>
</tr>
<tr>
<td>PSAN (KF)/DEFCH</td>
<td>5.98</td>
<td>&gt;0.8</td>
</tr>
<tr>
<td>PSAN (KF)/DEFTCH</td>
<td>5.39</td>
<td>&gt;0.8</td>
</tr>
<tr>
<td>PSAN (K₂Cr₂O₇)/DEFTCH</td>
<td>4.04</td>
<td>0.52</td>
</tr>
<tr>
<td>PSAN (KF)/CTPB</td>
<td>2.70</td>
<td>0.71</td>
</tr>
<tr>
<td>AN/CTPB</td>
<td>2.11</td>
<td>0.68</td>
</tr>
<tr>
<td>AP/DESBuH</td>
<td>20.8</td>
<td>0.63</td>
</tr>
<tr>
<td>AP/DESFH</td>
<td>21.1</td>
<td>0.64</td>
</tr>
<tr>
<td>AP/CTPB</td>
<td>8.2</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Sufficient to cast a practical 86 per cent solid loading. These considerations make the N-N-bonded polymers very attractive binders for AP propellants.

**Drawbacks of AP/HTPB Propellants**

As cited earlier the AP/HTPB is an excellent system incorporating many desirable features like high energy, strong binding characteristics, safety, easy handling, fairly high burn rate, and relatively low cost. It has been the most widely used solid propellant world over. Perhaps, the only serious drawback is that its products of combustion, which include gases like HCl and chlorine, cause atmospheric pollution and smoke. This has been a cause of concern in recent years, particularly at the launch cites, for large motors. For example, in each launch of the space shuttle, its solid propellant boosters exhaust 162.9 t of HCl and 24.1 t of chlorine in the atmosphere. Similar is the case with Ariane-5 with its two solid boosters each holding 237 t of propellant. Increasing concern for clean atmosphere in recent years calls for a compelling need for developing eco-friendly clean propellant systems. Apart from pollution concerns, smoky propellants are undesired for military applications. Dense smoke clouds, produced by AP propellants could lead to easy detection of the launch sites. Yet other reasons against AP propellants is their corrosive exhaust products (chlorine and HCl) and high flame temperature, which make them unsuitable as gas generators, used to start and drive gas turbines.

**Smokeless AN-based Propellants**

Ammonium nitrate is being reconsidered seriously as an oxidizer for solid propellants in recent years to overcome the problems associated with AP. It is a very cheap material and available in-plenty, as it is commonly used as a fertilizer, and in civil explosives. Its combustion products are totally innocuous and smokeless. Although AN-based propellants have been used as gas generators, AN has some unfavourable characteristics to suit as one-to-one substitute for AP. It is hygroscopic, and undergoes a crystal phase change accompanied by a volume change (expansion) at room temperature, due to which propellant grains develop cracks during storage. Also, AN propellants burn very slowly and have low energetics. Efforts made in recent years to improve these characteristics to make it a suitable propellant oxidizer, however, have largely been successful.
The near-ambient temperature phase (IV-III) transition, e.g., is no more a serious problem. In fact the crystal transformations of AN have been studied by numerous investigators using a variety of experimental techniques, as cited in our recent review. Our own observations have proved beyond doubt that the awkward phase (IV-III) transition could be arrested completely by co-crystallizing AN with an appropriate amount of a potassium salt. Interestingly the propellant samples having 80 per cent solid loading of the phase stabilized ammonium nitrate (PSAN) using potassium dichromate show almost nil expansion. Similarly, potassium dinitramide (KDN) is reported to have a dramatic phase-stabilizing effect. Moreover, AN phase stabilized with KDN is believed to give improved ballistic performance – increased thrust per unit time, reduced variability, and better predictability – compared with AN without KDN. Interestingly the hygroscopicity of AN is also reduced on co-crystallizing with K salts.

The problem of low burning rate of AN propellants has been tackled by different approaches. These include the use of catalysts, such as chromium compounds, addition of metals like Mg, use of a fast burning oxidizer like AP, and use of energetic binders, such as, azide polymers. Of these the approach based on energetic binders is most promising. However, many problems, like poor ignitability, combustion instability, thermal stability, inadequate mechanical properties, and high friction sensitivity associated with the azide polymer systems, has to be overcome prior to their use.

Interestingly, as shown in Table 3 the N-N-bonded resins have a significant influence on the burning rate of AN propellants. A substantial enhancement in the BR is observed when PSAN instead of AN is used. Burning rates close to the AP/CTPB system could be achieved when AN phase modified with potassium fluoride, and an N-N-bonded binder were used. These results parallel those obtained by Menke et al. on propellants based on PSAN having the azide binder. It is significant to note that the phase modification not only prevents the unwanted volume change around the ambient temperature, but also helps in enhancing the burning rate of AN propellants. Indeed the very significant enhancement in the BR has paved way for the feasibility of PSAN propellants in actual usage.

The last issue remaining pertains to the poor energetics of AN propellants. Seemingly, there is no way AN propellants’ energetics could be made at par with those based on AP, simply because it has higher heat of formation, density and oxygen balance than AN. However, choosing the right kind of binder can make some improvements possible. For example, CTPB or HTPB is not a suitable binder for AN propellants at least for two reasons. First the CTPB/AN propellants burn very slowly – at about one-fourth the rate of CTPB/AP propellants. Secondly, because of the low available oxygen in AN the amount of oxidizer needed for a stoichiometrically balanced composition is 94.2 per cent, which is too high a loading to cast in a grain shape. As a result the AN/CTPB propellant grains are always highly fuel-rich, giving much lower than the theoretical Isp. Recent investigations on AN propellants cast with N-N-bonded binders reveal that not only the burning rate is improved significantly as mentioned earlier, but the cast grains could be made that have an almost oxygen balanced composition, since a lower amount of AN (~85 per cent) is needed for complete (stoichiometric) combustion.

A comparison of the theoretical performance parameters of various propellants having different oxidizers, is made in Table 4. It is evident that the Isp of AN propellants processed with N-N-bonded binders is significantly higher. For example, at a practical 85 per cent AN loading, the theoretical Isp with CTPB binder is only 205.5 s; it could be enhanced to 222 s by using an N-N-bonded binder. The chamber temperature ($T_c$) and the characteristic velocity ($C^*$) are also appreciably higher. Even at equivalence ratio, $\Phi = 1$ (stoichiometric balance), the N-N-bonded resins give superior parameters than CTPB for AN systems. It is thus evident that the Isp of the AN systems can be improved upon by using appropriate binders. To sum up, these results clearly show that AN could be made to work, by using appropriate binders and phase modifiers, as a potential oxidizer for solid propellants.

Propellant compositions based on AP and ADN also give superior performance parameters with N-N-bonded binders at 85 per cent solid loading. Although better performance could be achieved with the polybutadiene binders at stoichiometric loading, it is not possible to achieve in practice without adversely affecting the mechanical properties. At practical solid loading the N-N-bonded resins give higher Isp than
Table 4 — Performance parameters of propellants at 85 per cent, and stoichiometric solid loading

<table>
<thead>
<tr>
<th>Binder</th>
<th>Oxidizer (per cent)</th>
<th>Φ</th>
<th>Isp (s)</th>
<th>Tc (K)</th>
<th>Mc</th>
<th>C* (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEFCH</td>
<td>AN (85)</td>
<td>1.10</td>
<td>219.2</td>
<td>2156</td>
<td>22.91</td>
<td>1358</td>
</tr>
<tr>
<td>DEFCH</td>
<td>AN (85)</td>
<td>1.10</td>
<td>222.0</td>
<td>2197</td>
<td>23.01</td>
<td>1371</td>
</tr>
<tr>
<td>CTPB</td>
<td>AN (85)</td>
<td>1.60</td>
<td>205.5</td>
<td>1622</td>
<td>19.45</td>
<td>1266</td>
</tr>
<tr>
<td>DEFCH</td>
<td>AN (89.8)</td>
<td>1.0</td>
<td>228.3</td>
<td>2370</td>
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<tr>
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<td>AN (91.0)</td>
<td>1.0</td>
<td>225.6</td>
<td>2296</td>
<td>23.59</td>
<td>1393</td>
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<tr>
<td>CTPB</td>
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<td>1.0</td>
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<td>2249</td>
<td>23.26</td>
<td>1384</td>
</tr>
<tr>
<td>DEFCH</td>
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<td>0.9</td>
<td>244.1</td>
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<td>1475</td>
</tr>
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<td>DESFH</td>
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<td>26.36</td>
<td>1482</td>
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<td>2770</td>
<td>24.12</td>
<td>1504</td>
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<tr>
<td>DEFCH</td>
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<td>247.4</td>
<td>3027</td>
<td>28.06</td>
<td>1488</td>
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<tr>
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<td>2941</td>
<td>27.59</td>
<td>1479</td>
</tr>
<tr>
<td>DESBuH</td>
<td>AP (87.1)</td>
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<td>244.7</td>
<td>2990</td>
<td>29.09</td>
<td>1481</td>
</tr>
<tr>
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<td>253.0</td>
<td>3046</td>
<td>26.78</td>
<td>1528</td>
</tr>
<tr>
<td>DEFCH</td>
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<td>1.1</td>
<td>259.4</td>
<td>3079</td>
<td>25.0</td>
<td>1585</td>
</tr>
<tr>
<td>CTPB</td>
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<td>1.6</td>
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<td>2625</td>
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<td>1549</td>
</tr>
<tr>
<td>DEFCH</td>
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<td>3058</td>
<td>25.27</td>
<td>1574</td>
</tr>
<tr>
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<td>ADN (92.7)</td>
<td>1.0</td>
<td>265.1</td>
<td>3061</td>
<td>24.42</td>
<td>1602</td>
</tr>
</tbody>
</table>

that could be obtained with CTPB irrespective of the oxidizer (AN, AP or ADN) used. This emphasizes the overall scope and usefulness of the N-N-bonded polymeric binders in solid propellants.

**Other Considerations**

**Aging**

Aging is one of the prime areas of concern. A solid propellant, particularly a combat rocket grain, has to be stored for several years before an event occurs when it has to be fired. Yet it must be kept in readiness all the time retaining its pre-determined characteristics, like the burning rate and pressure index, mechanical properties and structural integrity, unaltered. This is particularly difficult because the oxidizer and the fuel are in physical contact all the time and there is every likelihood they would undergo slow reaction between themselves, which could be further catalyzed by the additives like the BR modifiers, during storage. The grain could become porous if acted upon by moisture, or it could even change its characteristics by oozing out some of the plasticizer, if used. Thus, there are many factors that contribute to aging. But the first and foremost is that the proposed new binder must be least reactive with the oxidizer in the solid state.

There is no satisfactory method to evaluate a-priori the safe life of a solid propellant grain. Accelerated aging studies are carried out by monitoring BR or mechanical properties periodically at elevated temperatures, but they hardly correlate with the room temperature aging data. The only reliable way is to conduct a comprehensive study under storage conditions over a number of years and evaluate the safe life but it is time consuming, and so conveniently forgotten. As a consequence the reliability of the system becomes questionable. Very often, a new or modified propellant system performs as per the specifications in the initial testing stage but
its burning rate e.g., is changed drastically just in a few months storing time. In other words, a propellant meant to be good for 15 y may fail after, say 15 months only. For this reason, although several new energetic polymers have been evolved they have hardly been used in practice. Engineers put much faith in a proven system like the AP/Al/HTPB or CTPB, in view of the uncertain aging characteristics of the new system. Also, from the manufacturers’ point of view it is not beneficial to invest in a new system unless it is vastly superior, hazard-free and at the same time cost-effective.

Pot Life

For casting large solid boosters the propellant ingredients mixing (slurry making) is carried out in large batches using one or two ton mixers. It is imperative that the slurry after adding the curatives does not start setting in the mixer itself, but do so only after casting into the moulds. The time taken to gelling (pot life) should be long enough to permit the operations of proper mixing, de-aerating and vacuum casting. Methods available to lengthen the pot life include, choosing proper curatives and/or chain extenders, binder/curative ratio, mixing temperature, etc.

Solid Loading

Oxidizers like AP have just enough available oxygen to oxidize completely about 10 per cent of a hydrocarbon (CH₂) polymer (fuel). With so little amount of the binder it is very difficult even to make a uniform mix with nearly 90 per cent solids, leave aside a flowable slurry required to cast the propellant mix, in normal circumstances. This seemingly impossible task is made feasible to some extent, by using bimodal or even trimodal particle size mix. The sieved powder having fine and coarse particles, mixed in a fixed ratio, is added to the mixer in batches to achieve the maximum loading. To achieve maximum Isp, however, it is desirable that either the binder backbone should have ‘reactive’ (in combustion mode) linkages like N-N bonds, or groups that do not need extra oxygen for combustion, or the oxidizer must have higher available oxygen. Oxidizers like nitromium perchlorate and hydrazinium diperchlorate having much better oxygen balance are highly suited but they have their own drawbacks.

Conclusions

The emergence of specifically synthesized polymers has played a key role in casting large size solid propellant motors. Grains having desired structural strength and combustion characteristics could be successfully cast using functionally terminated viscous polymers. Efforts to develop propellant compositions giving high specific impulse ultimately led to the synthesis of hydroxyl terminated polybutadiene, a binder used currently worldover, in casting very large-size solid boosters. Continued search for binders suitable for specific purposes has resulted in several interesting systems. Of these the thermoplastic elastomers seem to be promising as these could also help in easy disposal of the aged propellants. The newly developed N-N-bonded polymers appear to be appropriately suitable for enhancing the performance parameters, and the burning rates of both ammonium perchlorate and ammonium nitrate based propellants. These binders seem to have particularly high potential for developing smokeless propellants based on phase-stabilized ammonium nitrate.

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References

JAIN: SOLID PROPELLANT BINDERS


