Composite Rocket Propellants Based on Thermoplastic Elastomer Binders

Vladica Bozic* · Boris Jankovski* · Marko Milos** · Bok Jik Lee***

ABSTRACT

The objective of this paper is to present new binder systems that can be applied in composite rocket propellants, to improve properties of these propellants not only for better performance, but also to reduce waste and pollution. These novel systems are based on the thermoplastic elastomer (TPE) binders, which consists of copolymers with the addition of a plasticizer, and additives. The effect of the novel TPE binder systems on the burning rate and mechanical properties of AP based propellants was studied. The results show that propellants based on the novel TPE binders have a better energy performance than today's workhorse hydroxyl terminated polybutadine/ammonium perchlorate propellant, exhibit a similar range of burning rate, possess appropriate mechanical properties, and exhibit good processing and aging characteristics at low cost.

Key Words: Thermoplastic Binders, Composite Rocket Propellants

1. Introduction

Modern solid propellants emerged in the early 1940's with the invention of composite propellants, which are basically heterogeneous mixtures of binder and oxidizer. First among the modern composite propellant was GALCIT 53, based on potassium perchlorate as oxidant, dispersed in a thermoplastic binder (liquid organic resin, asphalt). Limitations in operating temperature range, poor mechanical properties and low solids content precluded possible applications of this propellant, as well as of the later developed composite thermoplastic propellants based on polyvinyl chloride (Arcite propellants) and also polyisobutylene. These properties narrowed their application to sounding rockets, small motors and gas generators. The appearance of liquid prepolymers made possible the introduction of chemically cured (cross-linked or thermoset) binders in composite propellants (Fig. 1), which have better properties. These composite propellants find wider application as power sources covering the range from small rocket systems to large launch vehicles in space programs. At present, workhorse propellants [1, 2] are composite propellants based on hydroxyl terminated polybutadine (HTPB) and ammonium perchlorate (AP).

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* VEDA Design & Production Enterprise
** University of Belgrade, Faculty of Mechanical Eng.
*** LIG Nex1, PGM R&D Lab
Corresponding Author, E-mail: bjlee.snu@gmail.com

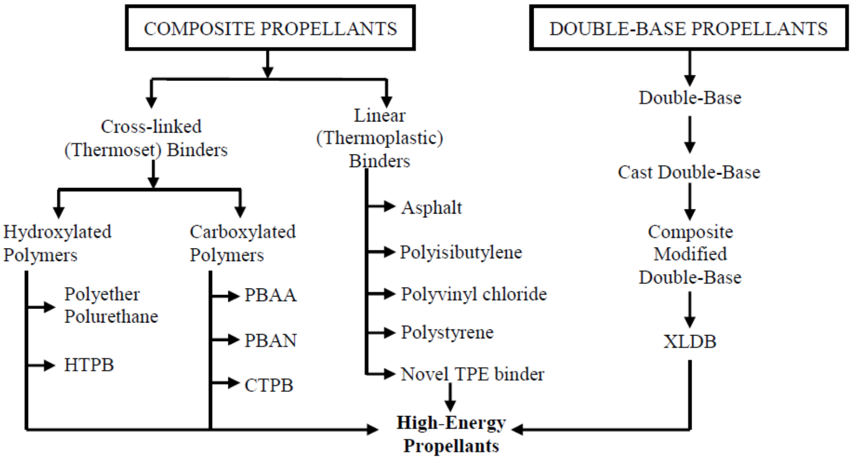


Fig. 1 Types of binders applied in solid rocket propellants

Cross-linked binders combine desirable high solid loading capability with the ease of processing leading to high specific impulse. Propellants with HTPB binder have relatively good density impulse, good safety and low cost. They are used either during the launch and/or flight phases, for small or large motors. The solid loading limit in these propellant formulations is between 86-88%, as the viscosity of slurry mixtures with low binder content is too high. But the practical use of those propellants indicated their disadvantages related to high line production of smaller propellant grains, more rigorous control, and slow preparation as moisture usually must be excluded during processing and storing. Also, casting is complicated by gassing and high viscosity, and bond failure and/or excessive voids often causes solid rocket motor malfunction that results in explosion or casing burn through, both of which results in loss of motor.

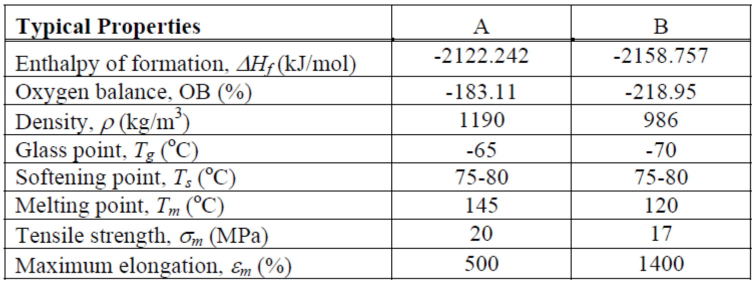
Novel applications as well as refinements of old ones require improvements in the properties of composite propellants. The rapid growth of the plastics industry has resulted in the development of new and different classes of polymers, which can be utilized in the manufacture of propellants [3, 4]. From this group of new polymers, two thermoplastic elastomer (TPE) binder systems are shown.

2. TPE Binders

Both thermoplastic binders are based on low cost ingredients, which are commercially available, thus yielding economical products. These compounds are based on high performance thermoplastic elastomers with the addition of plasticizer, and additives. The equivalent formula of the first binder system is $C_{43.199}H_{67.151}O_{4.946}Cl_{9.293}$, while for the second system is $C_{56.067}H_{77.686}O_{13.482}N_{2.371}$. Typical properties of these two TPE binders are given in Table 1.

Oxygen balances of both thermoplastic binders, which are about －200%, are higher in comparison with values for cross-linked binders like HTPB (about －300%), and this provides better combustion efficiency in rocket propellants.

Table 1. Typical properties of the TPE binders



Typical Properties	A	B
Enthalpy of formation, ΔH_f (kJ/mol)	-2122.242	-2158.757
Oxygen balance, OB (%)	-183.11	-218.95
Density, ρ (kg/m^3)	1190	986
Glass point, T_g (°C)	-65	-70
Softening point, T_s (°C)	75-80	75-80
Melting point, T_m (°C)	145	120
Tensile strength, σ_m (MPa)	20	17
Maximum elongation, ε_m (%)	500	1400

During the production of composite propellants using the TPE binder systems, if fillers were added at levels greater than 60% (which is the usual case in composite propellants), the TPE/oxidizer formulation could no longer be poured or cast, due to its extremely high viscosity. In this case, a different viable commercial processing technique would be used for loading high viscosity TPE-bound propellants. Processing techniques like extruding, injection moulding, two-roll milling, or pressing showed that the production of grains is possible from propellant compositions based on the TPE binder system which contain higher levels of solids. Propellant compositions using this binder system can accept up to 90% filler, depending on the type of process used. This high solid loading can be achieved with one size of solid oxidizer particles, from coarse to fine, or with a blend of two or more different oxidizer particle sizes (bimodal or trimodal). The temperature of the processing can range between 95~130℃, depending on the manufacturing method. Both case-bonded and freestanding grains can be produced.

As for all thermoplastic polymers, the polymerization reactions are completed before propellant manufacture begins, and the curing is eliminated from the manufacturing process of the propellants containing the TPE binders. Thus, the use of thermoplastic elastomers rather than cross-linked elastomers avoids the problems associated with pot-life and cure time. Also, the thermoplastic binder systems and their ingredients are almost insensitive to moisture and impurities in other ingredients.

Energy required to melt the thermoplastic elastomer is less than that required to cure or cross-link a chemically active thermoset propellant. Although the fusion temperature of the thermoplastic elastomer propellant formulations may be higher than typical cure temperatures of cross-linked elastomers, the time required for fusion is subsequently less than that generally required for curing. As a result, the electricity consumption, which during processing is necessary only for heating, can be decreased in comparison with processing techniques utilized in the production of thermoset propellants, which must be held at elevated temperatures for several days in order to cure properly. For example, the total cycle time of 8 hours are necessary in VACTEP plant to produce complete grain ∅135 mm with inhibition, compares with minimum 6 days cure time necessary for conventional thermoset propellants for the same grain diameter. About 20 hours are necessary to produce grain ∅500 mm from thermoplastic propellants.

In addition, the waste propellant (scraps or composition errors after processing) could be reformulated by heating, and then reprocessed

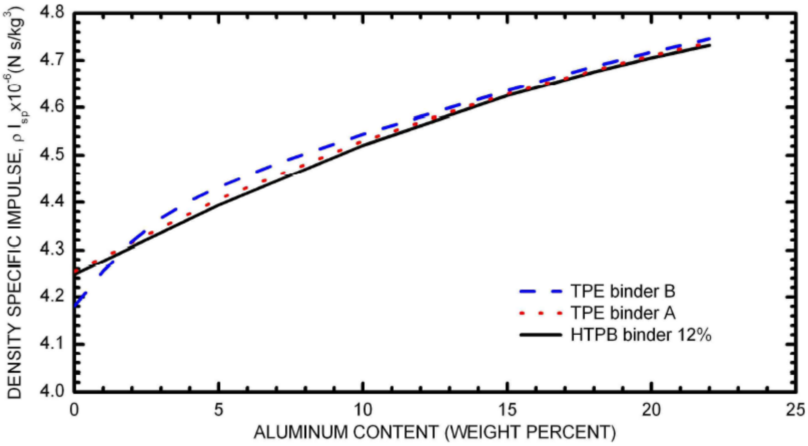


Fig. 2 Theoretical Isp of AP/Al composite propellants

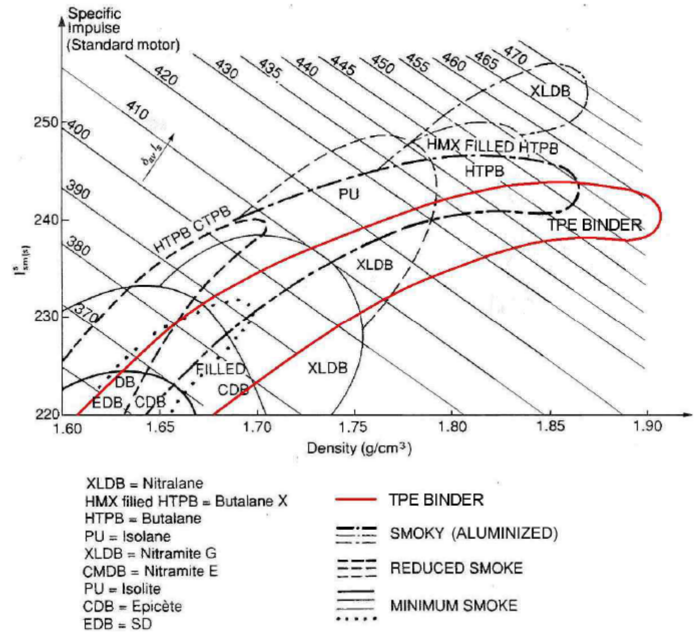


Fig. 3 Typical specific impulse and density for several solid propellant categories

or blended again to meet the specific requirements. Another advantage is that after mixing, the excess product can be reheated and used again, unlike the current cross-linked systems where the excess simply becomes waste. In this way, waste and pollution during processing of the grain can be reduced. Also, the ability to recycle or reuse decommissioned ordnance at the end of its useful life is possible through modification of the binder, plasticizers, or additives, and this capability can have a most significant effect on pollution prevention and waste minimization [5].

In order to illustrate the performance of the high-energy propellants based on the TPE binders in comparison with HTPB propellants,

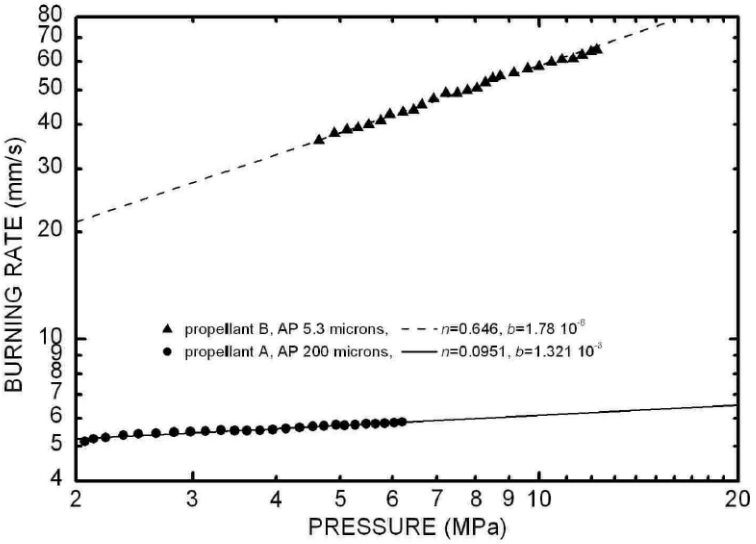


Fig. 4 Burning rate range of TPE binder systems

theoretical calculations have been performed with the COMBUS computer program [6, 7]. The calculated values of specific impulse (Fig. 2) are for adiabatic combustion at a rocket chamber pressure of 7 MPa, followed by isentropic expansion to 0.1 MPa.

The performance capability of a propellant usually is expressed as a specific impulse-Isp associated with a density-ρ, which product is called density specific impulse (ρ×Isp). Figure 2 shows the comparison of theoretical density specific impulse of TPE/AP propellants compared with HTPB/AP propellants for different Al loads. Theoretical density specific impulse is plotted versus aluminum content for these binder systems in propellant formulations for maximum possible solid loads. From Fig. 2 is obvious that the propellants based on TPE binder have higher density specific impulse than those of similar HTPB composite propellants. General conclusion is that regarding energy, propellants made from thermoplastic binders are comparable to composite propellants made by high-cost, cross-linked binders which are commonly in use; density of these propellants is slightly higher, giving higher density specific impulse and lower grain volume for the same total impulse (Fig. 3).

Composite propellants with TPE binders have the range of burning rate similar like HTPB propellants (Fig. 4). Also, these propellants have stable burning at lower pressures, even atmospheric. Mechanical and dynamic properties are good in comparison with other polymers applied in composite propellants, and retain these properties at low temperature (below -40℃).

Tensile stress is in range from 0.68~3.6 MPa, measured with the tensometer at a temperature +20℃ and a crosshead speed of 50 mm/min. Therefore, the tensile and tear strengths of the propellants with these TPE binders are better or comparable to the solid propellants with other engineering binders, while impact strength and flexibility characteristics are retained well at low temperatures (-40℃).

Storage life of thermoplastic propellants is practically unlimited due to good chemical stability of the binder systems. This permits long storage of grains when mounted in missiles, and offers less replacement costs which significantly reduce total costs of maintenances of missile.

3. Conclusion

Although the very first composite rocket propellant was thermoplastic, the development of composite rocket propellants in the past was mainly directed to thermoset polymers. The only exception was the development of Arcite PVC plastisol composite propellants. These propellants are synonymous for simple, low cost propellants with moderate ballistic, and poor mechanical properties. This paper reports about improvements achieved in the field of thermoplastic propellants. The current work illustrates that novel TPE binders has potential as a low-cost and “green” propellant binder. The propellants based on novel TPE binders have better energy performance than those of similar HTPB composite propellants exhibit a similar range of burning rate, and posses appropriate mechanical properties. As the storage life of these propellants is practically unlimited due to their good chemical stability, long storage periods are possible when this composition is used in missiles. The TPE binder systems are almost insensitive to moisture and the impurities in other ingredients in propellants. Various processing techniques can be used for producing grains of different forms and dimensions, from small to large scale. In the original patented process for producing grains, the inhibition process is part of the grain producing operation, which results in highly reliable grains, without cracks, bubbles, or other porosity. Application field of this class of propellants is wider than any other class. Replacing existing HTPB and other thermoset binders with novel TPE binders in composite propellants enables designers to increase the performance of rocket motors, and also set new trends in design.

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