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Asphaltic Thermoplastic Propellants

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A need has surfaced over the past several years for low-cost access to space. The two primary avenues for cost reduction are to lower propellant raw material costs and to lower processing costs. Thermoplastics and thermoplastic elastomers will help achieve these reductions. Several families of candidate thermoplastic materials have been evaluated, including acrylic resins and physically modified asphalts. These materials meet the criteria for continuous or alternate processing, are inexpensive, and have latent benefits with respect to oxidizer compatibility. The classes of thermoplastic elastomers explored consist of styrenic block copolymers. These materials provide cost benefits as well as desired mechanical and ballistic performance. These materials generally require a high-shear premix before propellant processing. The components required for ternary binder compositions are summarized, and current research is reported, and a view of proposed raw material costs and applications is given.

Nomenclature

I_{sp} = specific impulse
Tg = glass transition temperature

Introduction

CARTER[1] noted that the first thermoplastic solid propellant was formulated at the Guggenheim Aeronautical Laboratory of the California Institute of Technology (GALCIT) in June 1942. This propellant was used in jet assisted takeoff (JATO) units during World War II. The GALCIT 53 solid propellant was based on a paving asphalt plasticized with an aromatic oil and used potassium perchlorate as the oxidizer. Mixing was accomplished at 350°F, due to the autoignition temperature of the oxidizer, and the JATO cartridges were loaded manually, settled by bumping, and allowed to cool.

The GALCIT 53 composition burned at 8 in./s and gave an average exhaust velocity of 5315 ft/s at a chamber pressure of 1800 psi. This asphalt-based propellant had a variety of beneficial properties including excellent case bonding, low cost, and the potential of recasting or patching if a miscast was encountered. The recommended firing temperature range was set from 40 to 100°F. Above this temperature, the propellant flowed; below this range, the propellant became brittle and was prone to fracture. This limitation, based on mechanical properties, led to the demise of thermoplastic (TP) propellants and the introduction of chemical cure or thermoset propellants.

TP and thermoplastic elastomer (TPE) material systems have been used in other industries for decades. Specifically, the hot-melt adhesive and roofing industrial sectors have fine tuned the technology to provide low-cost, easily processable materials in high volume. Materials exist that process at 250°F and have a useful thermal range of −50–130°F, which are routinely used in these industries. The following sections describe the components used in the proposed TP-based propellant.

Viscosity-Graded Asphalt Cements

Asphalts may be defined as the residuum of crude oil processing, which are, by definition, the highest boiling fractions. They have an average molecular weight of roughly 1200 and contain approximately 2000 distinct chemical species.

An asphalt comprises an asphaltene and a maltene fraction. These are distinguished by their insolubility and solubility in n-heptane, respectively. The asphalt may be thought of as a colloidal system with the asphaltene and maltene phases being mutually immiscible. The asphaltene fraction contains high molecular weight, polar components, which are usually solid at ambient temperatures. The n-heptane soluble maltene fraction consists of three types of species: resins, aromatics, and saturates. The resins are species soluble in a mixture of benzene and ethanol and act as emulsifying agents between the asphaltenes and the aromatics and saturates. The aromatics are oils soluble in n-pentane and are composed of lower molecular weight aromatic hydrocarbons. The saturates are benzene-soluble lower molecular weight paraffins and naphthenes.

The asphalts used in this study are viscosity graded and are identified as asphalts cement- (AC-) X where X is defined as the viscosity in hectopoise units measured at 140°F. Figure 1 shows viscosity as a function of temperature for all of the asphalts used. Hence, an AC-20 asphalt stock would be one whose viscosity at 140°F is 2000 P. The range of asphalts under study include AC-2.5, AC-5, AC-10, AC-20, and AC-40. Also under consideration are propane dewaxed asphalts (PDAs), processed to contain minimal saturates, and crude resins (CRs), which are treated to retain only resins and aromatics.

TPEs

Block copolymers such as styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS) systems have been used in the hot-melt adhesive industry for several years. These materials, manufactured by the Shell Chemical Company and Fina Oil Company, have the advantage that they are elastomeric within their operating range and TP above their hard-block glass transition temperature Tg. The soft-block segments allow flexibility down to −85°F in the case of butadiene and −65°F in the case of isoprene. Above 250°F, either polymer can be processed as a conventional TP as long as moderate to high shear is applied. For this reason, the SBS and SIS materials cannot be used neatly in propellants using conventional processing.

It is possible to formulate binders based on these elastomers in conjunction with a suitable plasticizing agent, such as a naphthenic or paraffinic oil, that associates with the soft-block segments. A tradeoff is in place between elastomer mechanical properties and processing properties using this approach.

Alternative processing, such as extrusion, allows the use of the neat elastomers because this method allows for high shear.

Acrylic TP Resins

Acrylic polymer resins have been traditionally used for coatings due to their excellent weatherability and ultraviolet radiation stability. These resins are long-chain polymers of acrylic and

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Table 1 Theoretical sea level specific impulse values as related to asphalt, asphalt/TPE, and TP resin type

Binder species	Maximum I_{sp}, s	% Binder	% Aluminum	% AP
AC-5	261.23	10	22	53
AC-10	261.26	10	22	68
AC-20	261.14	10	22	68
PDA	261.14	10	22	68
CR	260.72	10	22	68
AC-5/TPE	261.06	10	22	68
AC-20/TPE	261.16	10	22	68
PDA/TPE	261.05	10	22	68
B-66	262.46	14	24	62
B-72	262.89	16	22	62
C-10LV	256.43	20	26	54

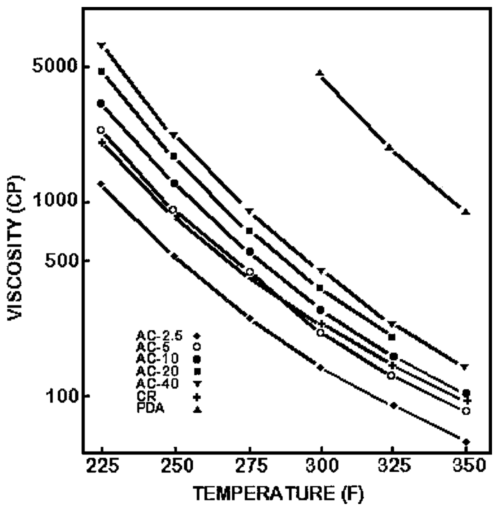

Fig. 1 Viscosity as a function of temperature for asphaltic systems.

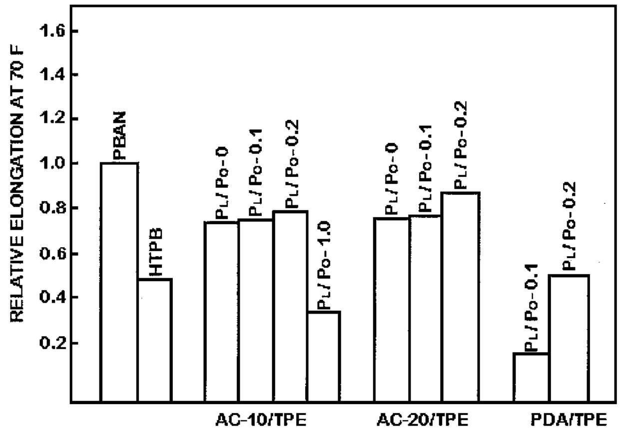

Fig. 2 Uniaxial elongation values for three families of asphalt/TPE propellants at 70°F.

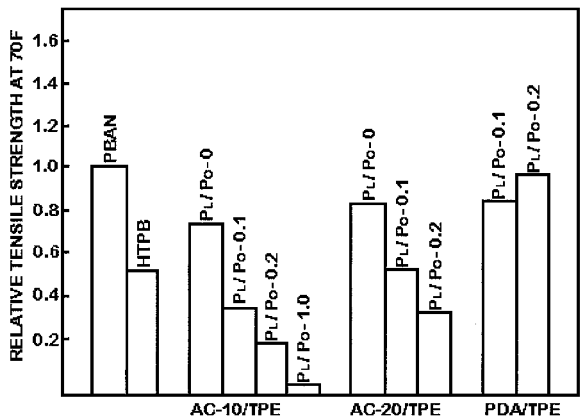

Fig. 3 Uniaxial tensile strength values for three families of asphalt/TPE propellants at 70°F.

methacrylic esters.[2] Low carbon-number polymethacrylates generally have a high tensile strength (5,000–10,000 psi) and a low elongation (2–8%). Lower tensile strengths (20–1000 psi) and higher elongations (750–2000%) are obtained with low carbon-number polyacrylates. A combination of these properties may be obtained by generating a copolymer of the cited species. These copolymers, trade-named ACRYLOIDS by Rohm and Haas, are used to yield paints and coatings with high durability over a wide temperature range.

Although these materials are true thermoplastics, the polymethacrylate portion of the copolymer generally yields a melt processing temperature of 250–350°F, too high for propellant binder use. Typically, these materials are solution processed, which would also be generally unsuitable for grain manufacture.

Current Research

To date, asphalts have been commercially graded based only on physical properties, due to the variablity of the crude stock and large number of chemical species present. This was originally viewed as a detriment from a propellant standpoint because the ballistic properties were thought to rely heavily on the discrete chemical composition. Table 1 shows the optimum theoretical specific impulse I_{sp} calculated for several asphalts, asphalt/TPE systems, and TP resins. It is seen that the I_{sp} values do not differ by more than 0.2% in the case of asphalts, 0.04% in the case of asphalt/TPE systems, and 2.5% in the case of TP resins, indicating the insensitivity of the specific impulse within a wide variety of homologs. Variability within a specific viscosity grade of asphalt will, therefore, lead to extremely small perturbations in specific impulse. The I_{sp} values between types (asphalt, asphalt/TPE, or TP resins) also indicate no inherent energy penalty. The density of cured hydroxyterminated polybutadiene (HTPB) is 57 lb/ft^3 and that of an average asphalt is 68 lb/ft^3. This leads to a significant improvement in density I_{sp}.

Asphalts have been identified as candidate propellant binders due to their low cost and defined ballistic properties. Viscosity grading makes possible a range of defined gumstock processing specifications. As already mentioned, the original problems inherent to asphalt propellants were their poor physical properties or narrow temperature operating range. The purpose of this recent in-house research effort is to develop a novel propellant binder with improved physical properties using a physically modified asphalt.

Figure 2 shows uniaxial elongation measured at 70°F for three families of asphalt/TPE propellants with varying plasticizer ratios; the plasticizer used was a naphthenic hydrocarbon resin. Polybutadiene–acrylonitrile (PBAN) and HTPB propellants are also shown as a comparison. All propellants consist of 18% 6-μm aluminum, 45% 200-μm ammonium perchlorate (AP), and 22% 25-μm AP. The remainder is the binder or binder/plasticizer. An elongation value of 18.1% is defined as the reference number against which all other elongation values are derived. It is seen that the AC-10 and AC-20 derived materials have roughly 70% the elongation of the PBAN propellant at lower plasticizer loadings. The effect of binder performance is clearly seen in the HTPB case, where the elongation value is 43% that of PBAN.

Figure 3 shows a summary of uniaxial tensile data measured at 70°F for the families discussed earlier. A tensile value of 185 psi is defined as the reference state for the formulated PBAN propellant. For a given plasticizer loading, the tensile values increase with increasing asphalt viscosity grade. In the lower grades, tensile values decrease with increasing plasticizer content, as expected. Again, the bonding agent effect is seen with the HTPB data, dropping to 46% of the value of PBAN.

Figure 4 is a graph of uniaxial modulus as a function of plasticizer ratio, taken at 70°F. A modulus value of 1710 psi is defined as the reference state for the formulated PBAN propellant. The decreasing

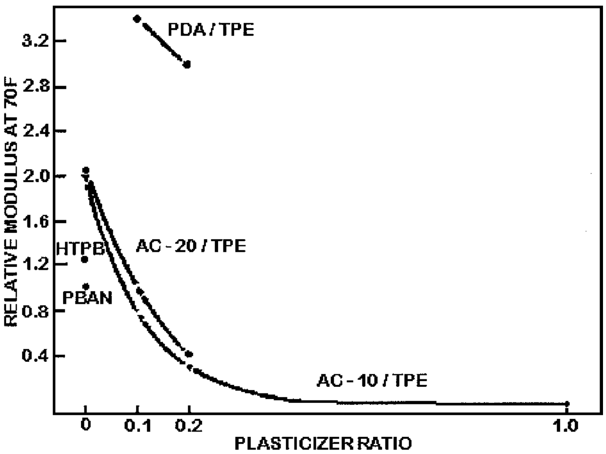

Fig. 4 Uniaxial modulus as a function of plasticizer ratio at 70° F.

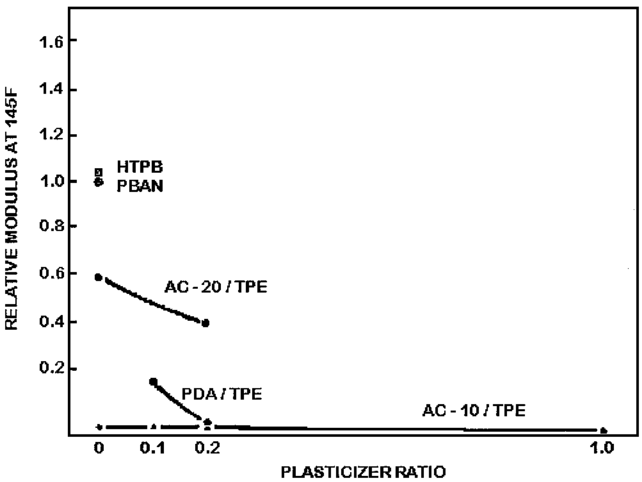

Fig. 5 Uniaxial modulus as a function of plasticizer ratio at 145° F.

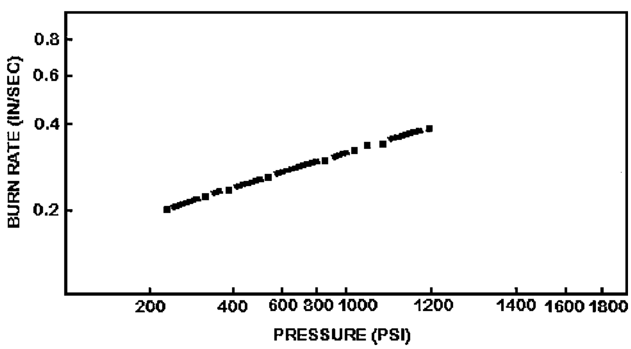

Fig. 6 Burn rate as a function of pressure for a PBAN formulated system; data obtained by 2 × 4 motor method.

functionality is evident within all three families of asphalt/TPE propellants. The modulus increases with increasing asphalt viscosity grade, with the AC-10 derived grade being closest to the PBAN standard. The HTPB formulation exhibits a 25% greater stiffness than the PBAN propellant.

Figure 5 is essentially the same as Fig. 4, except the data were obtained at 145°F, and a reference state of 1213 psi is defined for the PBAN propellant. The modulus values drop dramatically in most cases. The AC-20 data show, at best, 60% the value of the PBAN standard.

Figures 6 and 7 show burning rate as a function of pressure for the formulated systems containing PBAN and HTPB. Figures 8, 9, and 10 show similar graphs for the asphalt/TPE propellants using AC-10, AC-20, and PDA asphalts, respectively. All burn rates are

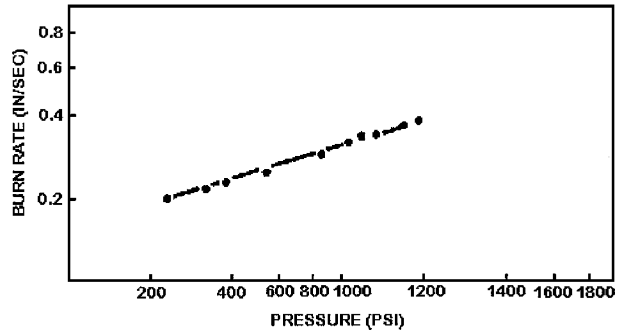

Fig. 7 Burn rate as a function of pressure for a HTPB formulated system; data obtained by strandburner method.

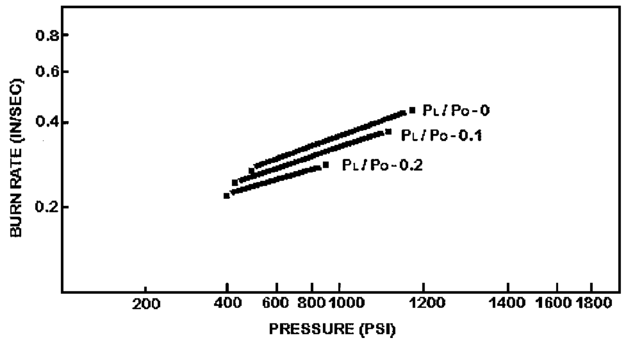

Fig. 8 Burn rate as a function of pressure for a AC-10/TPE propellant; data obtained by 2 × 4 motor method.

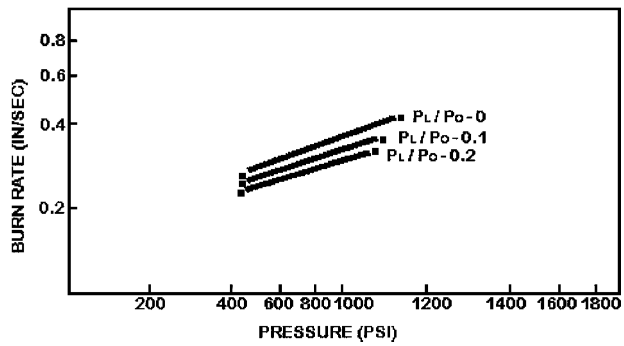

Fig. 9 Burn rate as a function of pressure for a AC-20/TPE propellant; data obtained by 2 × 4 motor method.

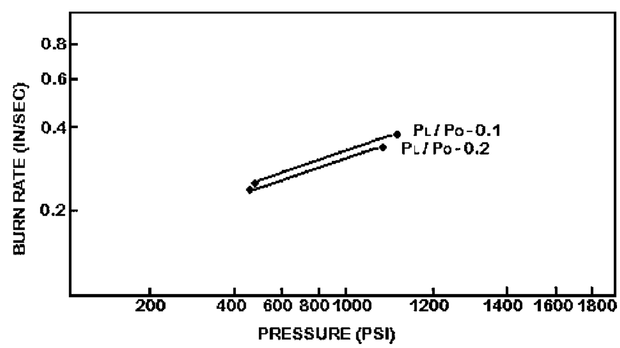

Fig. 10 Burn rate as a function of pressure for a PDA/TPE propellant; data obtained by 2 × 4 motor method.

seen to be similar with respect to magnitude and slope, with the slope decreasing with increasing plasticizer ratio.

The preceding discussion shows the asphalt/TPE propellants to be comparable to the PBAN standard data with the exception of high-temperature modulus. It is for this reason that small amounts of TP resins (ACRYLOIDS) are included in the formulations.

An intimate physical mixture of an asphalt, TPE, and ACRYLOID is expected to yield a gumstock with the processing characteristics of the asphalt, the low-temperature flexibility of the TPE, and an enhanced modulus due to the ACRYLOID. Asphalts and KRATON TPE material are generally miscible up to about 40% by weight of TPE before phase separation occurs if the asphalt contains a suitable amount of aromatic and/or saturate fractions. Asphalts and ACRYLOIDS are miscible to about 50% by weight of ACRYLOID if the asphalt contains high enough fractions of associating asphaltenes and/or resins. The strength in using asphalt as the major binder constituent lies in its colloidal properties, namely, two fractions will disperse in ACRYLOID while the remaining two fractions will solubilize the TPE.

Gumstocks are made in the laboratory by first dispersing the asphalt, TPE, and ACRYLOID separately in toluene. These dispersions are then mixed thoroughly, cast as a slab, and then dried in a vacuum oven at 175°F. The finished gumstock slab is then ready for testing.

Viscosity at process temperature is the first parameter to be explored as a function of this subspace. The goal for the processing viscosity is to be lower than 200 P at 250°F.

Asphalt materials contain a sizable percentage of aromatic and polar organic materials. For this reason, they case bond quite well to metallic substrates and inorganic crystalline oxidizers.

Raw Material Costs

The goal of this research effort is to develop a TP-based propellant for use in large launch vehicles. The market price for asphalt currently ranges from \$0.08–\$0.12/lb. The supply of this material is quite extensive because it is used in high-volume applications such as paving and roofing. KRATON TPEs sell for roughly \$0.60/lb and ACRYLOIDS range from \$1.00 to \$1.20/lb. A successful admixture of these materials should cost roughly \$0.25/lb.

Depending on the results obtained in the ternary-space evaluation, these materials may find uses in the more severe environments of air-launched and tactical missiles. The excellent case bonding and propellant tailoring characteristics would seem to indicate this.

Summary

The current work has indicated that physically modified asphalts have potential as low-cost propellant binders. Data indicate that it is possible to produce a two-component thermoplastic binder by means of an elevated-temperature, high-shear mixing process. This asphaltic/TPE binder behaves similarly to the current PBAN binder with the exception of high-temperature modulus.

It has been demonstrated that a ternary system comprising an asphalt, TPE (KRATON), and TP (ACRYLOID) can be successfully formulated by means of a solvent moderated preblend.

References

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[2] Brendly, W. H., Jr., "Fundamentals of Acrylic Polymers," Univ. of Detroit Polymer Conf. Series, 1973, pp. 1–9.