

Design Principles of Advanced Solid Propellants

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A computer-aided approach for primary optimization of propellant formulations is described. The computer code includes a database containing information of approximately 1000 propellant components and 1600 combustion products. Possible ways of designing the advanced components of composite solid propellants (binders, plasticizers, curative agents, and oxidizers) are considered. The physicochemical and physicochemical behavior (and related phenomena) of materials with a high content of disperse components, determined by rheology and mechanical and kinetic parameters, is analyzed in detail.

Nomenclature

| | |
|------------------|---|
| $[A]$ | = mechanical parameter of system, Eq. (6) |
| A_i | = stressed-state parameters depending on the loading H_i acting in calculated zones of construction, Eq. (7) |
| a_i, b_i | = characteristics of influence of a certain component of a composition on mechanical properties of composition, Eq. (6) |
| C_i | = concentration of the i th component in combustion products |
| f | = function symbol, Eq. (6) |
| g | = gravity acceleration |
| I_{sp} | = specific impulse |
| K_i | = function characterizing influence of temperature and time of loading, stress type, and aging on limiting mechanical parameters δ, ϵ , Eq. (7) |
| k | = nozzle-averaged isentropic coefficient |
| M | = averaged molecular mass of gases in combustion chamber |
| m_e | = final mass of rocket |
| m_0 | = initial mass of rocket |
| n_i | = characteristic of influence of a certain component of a composition on its mechanical properties |
| p | = pressure |
| p_a | = pressure at nozzle exit section |
| p_c | = pressure in chamber |
| R | = universal gas constant |
| T_g | = gas temperature in combustion chamber |
| U_f | = enthalpy of propellant formation |
| $U_i(T)$ | = enthalpies of combustion products |
| V | = volume |
| V_{max} | = maximum rocket velocity |
| w | = characteristic of system filling (depends on type, size, and shape of filler particles) |
| α | = exponent, Eq. (3) |
| δ | = deterministic criterion, Eq. (7) |
| ϵ | = deformation |
| $\dot{\epsilon}$ | = rate of deformation |
| μ | = viscosity |
| ρ | = propellant density |
| σ | = tensile stress |
| φ | = volume fraction of filler |
| φ_m | = maximum of volume fraction of filler |
| χ_i | = mass portion of main components of composition |

Introduction

DURING the last decades composite solid propellants (SP) have gained widespread acceptance as autonomous energy sources. The possibility of wide variations of compositional, energetic, and ballistic parameters of SP makes it possible to use the propellants not only in rocket propulsion, but also in oil and gas production, fire-fighting and life-saving equipment, and generators of gases with given parameters (composition, pressure, and temperature), etc. Initially, composite SP, which were used in solid propellant motors for multistage rockets, had to satisfy severe requirements. The design of composite SP is based on current achievements of fundamental and applied sciences.

Among the requirements imposed on SP are the following:

1) High-energy characteristics determined by the value of specific impulse I_{sp} : increasing I_{sp} extends the flight range and increases the payload value. This follows directly from the Tsiolkovskii equation for the maximum (ideal) rocket velocity V_{max} :

$$V_{max} = I_{sp} g_0 \ln(m_0/m_e) \quad (1)$$

2) High density: the higher the density, the greater the value $\ln(m_0/m_e)$ due to relative reduction of rocket dimensions and rocket case mass m_e at a given mass of the propellant.

3) Burning rate of the propellant should be independent of or weakly dependent on pressure and temperature, which also decreases m_e due to diminished assured storage of propellant and case strength.

4) High mechanical characteristics that provide high loading of rocket motors and enhance the mass perfection parameter m_0/m_e .

5) Long-time stability of performance parameters of solid rocket motors (SRM) in storage, provided by means to control (or exclude) low-temperature phase transformations and chemical reactions in the propellant.

The previous requirements are frequently in mutual contradiction. For example, it is impossible to get the highest values of I_{sp} and density simultaneously by variation of propellant formulation. It is known that I_{sp} increases with decreasing molecular weight of combustion gas products. The value of molecular weight can be reduced by increasing the amount of hydrogen-containing compounds. However, this usually decreases the propellant density.

Using Eq. (1) and keeping the maximum rocket velocity constant, one can obtain the relationship:

$$I_{sp} \cdot \rho^\alpha = \text{const} \quad (2)$$

$$\alpha = \frac{m_0 - m_e}{m_0 \ln(m_0/m_e)} \quad (3)$$

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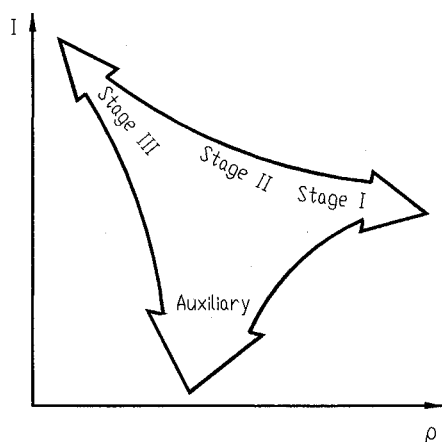


Fig. 1 $I_{sp} - \rho$ relationship for SPs used in solid rocket boosters and auxiliary motors.

It follows from Eq. (2) that the contributions of I_{sp} and density to the maximum rocket velocity are different and depend on rocket design. For typical three-stage ballistic rockets, an analysis has shown α to be 0.70, 0.30, and 0.20 for the first, second, and third stages, respectively. High-density propellants are beneficial in the first stages, while propellants of lower density and higher I_{sp} are more efficient in the upper stages. Thus, for the most efficient operation of rocket motors it is desirable to use particular propellants in each stage. The design of new composite SP for conventional SRM is preceded by the calculation and optimization of thermodynamic and energetic characteristics.

For SP designed for other purposes (pressure accumulators, generators of high-temperature plasma, generators of IR radiation, pure gas, etc.), calculations of parameters and optimization of propellant formulations are performed with respect to other characteristics. Therefore, the specific impulse and mass density values for these compositions can be lower (Fig. 1).

Thermodynamic Calculations of SP Parameters

Thermodynamic calculations were accompanied by the development of special models, methods, and programs that were used for the design, optimization, and refinement of propellant formulations.

A generalized scheme of primary computer-aided optimization of propellant formulations are as follows: selection of decomposition products; computation of thermodynamic functions; determination of physicochemical data for components and formulations from database; computation of enthalpies of formation of components and compositions; computation of component and composition densities; selection of data for taking into account the extent to which gases do not follow the perfect-gas law; determination of decomposition products; computation of thermodynamic characteristics of combustion products; computation of thermophysical characteristics; computation of electrophysical characteristics; computation of variations in specific impulse loss; computation of variations in flight distance, overall mass, payload mass, and other generalized characteristics; computation of detonation velocity; primary estimation of thermal stability and compatibility of components; primary estimation of catalyzing and inhibiting abilities of components; estimation of possible existence of nonequilibrium particles of soot and other condensed products at moderate and low temperatures; primary estimation of reaction incompleteness at moderate and low temperatures; primary estimation of parameters of exhaust gases; determination of thermodynamic characteristics and chemical composition of combustion products and of substances arising in interaction of combustion products with environment; and the accumulation of computation results

and their output by special devices and memory systems (printer, display, tape recorder, etc.).

The computer database currently contains information on almost 1000 propellant components and formulations, and on 1600 combustion products. The computation code is extensively used in designing new propellant components, estimating the potentialities of available components, and in designing and optimizing novel propellants and charges based on these propellants. The code incorporates corrections of the main parameters, obtained from comparison with prototype propellants. After the preliminary design of a propellant formulation, the analytical and numerical refinement of the parameters and experimental investigations (when necessary) are performed within narrow ranges of component variations.

As shown above, the specific impulse is one of the most important characteristics in determining the increments of flight distance, payload, and other parameters. The one-dimensional gasdynamics theory suggests the following expression for calculating the specific impulse:

$$I_{sp} = 4.562 \sqrt{(R/M) T_g [k/(k-1)] \{1 - (P_a/P_c)^{(k-1)/k}\}} \quad (4)$$

From this equation, it follows that the calculated specific impulse increases with T_g and decreases with M . I_{sp} also increases with decreasing k .

From the law of conservation of energy we have

$$\sum_i n_i \Rightarrow C_i(p, T) U_i(T) - U_f = 0 \quad (5)$$

Equation (5) suggests that the temperature of products in the combustion chamber increases with propellant formation enthalpy and concentration of gaseous combustion products with the least possible enthalpies. Therefore, it is useful to include metal or metal-containing components (in particular, aluminum, whose combustion product, aluminum oxide, has low enthalpy) in propellant formulations. It is also profitable to use propellant formulations that include metal hydrides and binders with high concentrations of hydrogen, carbon, nitrogen, and other elements with the highest possible formation of enthalpies. For example, the compositions based on ammonium perchlorate (AP) and aluminum usually contain rubber binders with high hydrogen and carbon content. Increasing total metal and oxidizer content up to 90–95% (see Fig. 2) and reducing rubber binder to 10–5% result in high I_{sp} values.

Real propellant formulations can differ from optimum formulations (calculated thermodynamically) by having less metal content, which reduces the loss in I_{sp} due to incomplete metal combustion and two-phase flow, as well as by the high content of the binder (for optimization of the rheological parameters of propellant mass during manufacture).

The binder content can be increased at constant I_{sp} by substitution of a certain amount of heterogeneous oxidizer with an energetic (containing oxidizing elements) binder. The data of Fig. 3 confirm the possibility of designing high-energy compositions containing 15–20% energetic binder. A number of advanced composite SPs with extremely high delivered performance have been designed by this method in Russia for lower-, intermediate-, and upper-stage SRMs.

Along with the main components, real propellants contain up to 1.5–2% of combustion additives serving different functions (curative agents, surface active substances, catalysts, stabilizers, etc.), which offer considerable possibilities for the design of new compositions. As a rule, the additives are energetically less effective than the binder. Their introduction into a propellant formulation can reduce I_{sp} by 2–3 s. Propellant energy can be enhanced by excluding the effect of additives. Therefore, the selection of additives is a subject of special research that may involve a purposive synthesis.

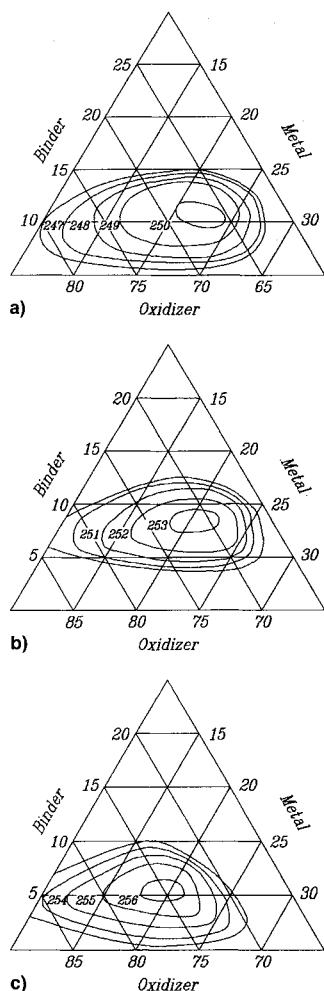


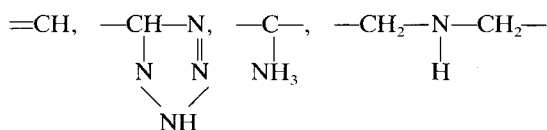
Fig. 2 I_{sp} (s) as a function of AP/binder/metal content (weight %); energetic additive, %: a) 0, b) 20, and c) 40.

Development of the Components of Composite SP

Fuel Binders

A very important component of composite SP is the polymeric binder, which performs a number of functions: provides the propellant mass rheology during propellant processing, provides the mechanical properties of propellants needed for rocket performance, and allows the formation of combustion products of low molecular mass.

High-molecular polymers with optimum molecular mass distribution (MMD) along with low-molecular plasticizers meet the above requirements. The higher energy of polymer and plasticizer molecules is attained by the highest possible hydrogen concentration and the absence of oxidized (even partially) atoms of carbon and other elements. An example of such a binder is butyl rubber of the general composition $(-CH_2-)_n$ plasticized by low-molecular compounds. A number of butyl rubber fuel binders (FBs) have been designed. The energy and density parameters I_{sp} , ρ of composite SP can be enhanced via complication of the polymer molecules through the addition of certain atomic groups such as



The use of such polymeric binders together with corresponding plasticizers allows the effective specific impulse to be enhanced by 3–6 s.

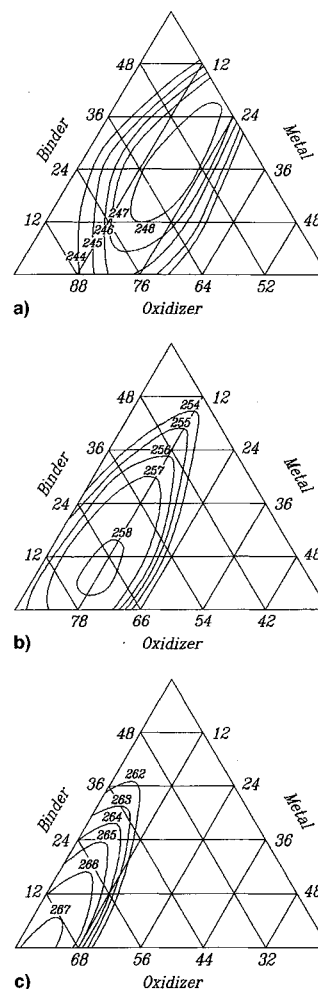


Fig. 3 I_{sp} (s) as a function of AP, active (energetic) binder and metal content (weight %); energetic additive, %: a) 0, b) 20, and c) 40.

Another method used to enhance the energetics of a composite SP is adding oxidizing-atom groups to binder molecules. An example of this type of binder is CVEI, a copolymer of vinyl ether of ethylene glycol mononitrate (EGMN) and isoprene. In development of the synthesis procedure for CVEI, a number of problems were solved: catalytic vinylation and high purification of EGMN, acid-catalytic polymerization of the nitrate monomer, purification of CVEI, and stabilization of manufacturing processes to obtain the rubber with certain molecular mass distribution. Whatever the polymeric binder, its molecule must contain a minimum of necessary double-bond links or active functional groups of atoms that allow formation of a spatial structure. However, the excessive content of reactive elements in the molecular chains of polymeric binders can decrease propellant stability.

Plasticizers

The rheology of uncured propellants is improved by the introduction of plasticizers (up to 70–80% FB mass). The contribution of plasticizers to the energy content of composite SP is larger than that of polymeric components of FB. Therefore, the plasticizers must meet strict demands as to their molecular structure, which should contain a large number of effective functional atom groups.

Of interest are nitroester (NE) plasticizers such as ethylene glycol dinitrate, nitroglycerin, and nitroisobutanetriol trinitrate. The very high density, $\rho = 1.64 \text{ g/cm}^3$, of the latter is not typical for NE. The widespread use of NE as plasticizers made it necessary to develop high-safety and automated technologies based on small-size permanent-action devices for the

Table 1 Physicochemical parameters of the available quinol esters

| Curative agent | R | R ¹ | R ² | Time of BR ^a polymerization at 60 deg, days | Solubility in TO, ^b g/100 ml (temp., °C) |
|----------------|----------------------------------|--------------------------------|-------------------------------|--|---|
| QE-1 | C(CH ₃) ₃ | H | H | 8 | 0.3 (20) |
| QE-2 | OCH ₃ | H | H | 3 | 0.2 (40) |
| QE-8 | CH ₃ | H | H | 6 | 0.5 (40) |
| QE-4 | C(CH ₃) ₃ | H | H | 7 | 0.25 (40) |
| QE-10 | C(CH ₃) ₃ | CH ₃ | C ₂ H ₅ | 12 | 0.916 (60) |
| QE-25 | C(CH ₃) ₃ | C ₂ H ₅ | H | 10 | 1.6 (40) |
| QE-153 | C(CH ₃) ₃ | OC ₂ H ₅ | H | 8 | 21.0 (20) |

^aButyl rubber. ^bTransformer oil. ^cQuinol ester.

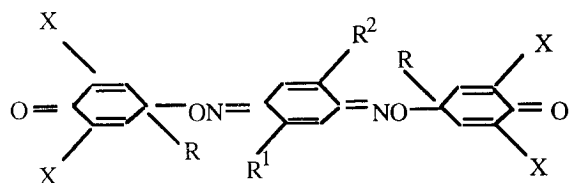
production of these materials, which involves nitration, separation of NE from nitrating agents, repeated washing, and stabilization of final products.

Aliphatic nitramines are, at present, very promising candidates for plasticizers. The synthesis and treatment procedures for these compounds have been developed sufficiently.

Curative Agents

The SP components of this group are responsible for the formation, in the presence of a heterogeneous filler, of a three-dimensional net (3DN) of plasticized polymeric binder. The concentration and uniform distribution of the 3DN are extremely important in gaining reproducible mechanical characteristics of SP charges.

From this point of view, the ability of curative agents to dissolve in binder and to perform their functions at certain temperatures (polymerization point) is very important. In addition, curative agents must be extensively oxidized, thus minimizing the I_{sp} decrement. Purposive investigations have resulted in the synthesis of quinol esters, curative agents of the desired structure and properties (Table 1):



where X = C(CH₃)₃.

Quinol esters (QE) act through the double bonds of the rubber. QEs provide low temperature of formation of three-dimensional polymers and make it possible to obtain chemically stable high-elasticity compositions. QEs weakly affect propellant energy.

Another class of curative agents acting through the active functional groups in the polymer chain is represented by individual and composite epoxy materials. Among the most interesting and well-proved epoxy materials is the newly synthesized epoxy hydantoic resin EH-10. Use of this resin essentially enhances the mechanical properties of composite SP, not only because of the optimal concentration of 3DN, but also because of the more active participation of filler in the 3DN formation owing to increased adhesion of FB to crystals.

Special Additives

Some special additives are surface-active substances (SAS) that improve propellant rheology. They comprise a quite extensive class of amine compounds, esters of phosphoric acid, etc., which decrease propellant energetics. Other additives are synthesized combustion catalysts and stabilizing agents. The molecules of these compounds can also contain heavy metals and involve ether and ester bonds. Therefore, their negative contribution to the propellant energy is even more pronounced.

Oxidizers

The oxidizers most generally employed are nitrates and perchlorates. The solid propellants for boosters usually contain ammonium nitrate or ammonium perchlorate. The latter provides the highest energetic characteristics of SP. Complex physicochemical and crystallographic studies have proved AP to be the most efficient oxidizer. However, its combustion products (perchloric acids, chlorides, and hydroxy chlorides) have hazardous effects on the environment and human health. Therefore, the attention of researchers is now focused on chlorine-free oxidizers, among which are salts of nitric acid (e.g., ammonium).

Using the energetic binders as SP components makes it possible to employ different types of oxidizers, e.g., compounds involving nitramine groups. Real propellants with such oxidizers exhibit high ballistic efficiency, and their combustion products are much less ecologically hazardous.

The mathematical simulation of molecular structures provides possibilities for the synthesis of new oxidizers with high enthalpies of formation and densities ($\rho \approx 2.0$ g/cm³).

Research on oxidizers based on all of these approaches is currently in progress at many laboratories.

Rheology of Materials with High Content of Disperse Components

The rheological characteristics of uncured composite materials are the most important parameters in the manufacture of certain products and units. These characteristics depend on intrinsic rheological properties of disperse medium, the presence of SAS, the volumetric content of filler ϕ , the filler grain-size distribution, and the presence and effects of 3DN, etc.

The rheology of systems with low contents of disperse components has received a great deal of study. However, the same cannot be said concerning the rheological behavior of polymers with high concentrations of disperse materials. Therefore, we recognized the need to study the rheology of uncured propellants with a high volumetric content of disperse components ϕ (up to 80%). Representative and sufficiently accurate mathematical models have been developed.

The models were employed in predicting the fluidity (shear rate) of materials depending on composition, environmental conditions, and on the design features of real production equipment and engines. A computer-aided technique was developed for designing the processing procedures for propellants and, in general, for composite materials (CM).

Experimental data show that the absolute values of the rheology characteristics of a CM depend strongly on insignificant changes in its chemical composition or in the fraction ratio of the disperse filler. An analysis of a flow of incompressible disperse materials yielded the important conclusion that the viscosity ratio of the system (i.e., uncured propellant) and pure binder μ/μ_b depends on the ratio of a given volume fraction of filler ϕ in the system to the maximum possible volume fraction of filler ϕ_m with the same grain size (at the closest packing).

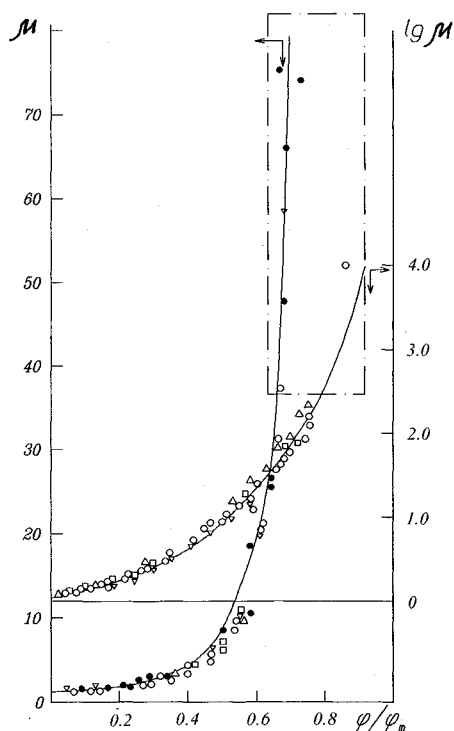


Fig. 4 Viscosity as a function of the relative volume fraction of disperse filler for different propellant formulations. The domain bounded by dash-dot lines corresponds to real propellants.

Experimental data on real and model propellants with various fillers are applied to the theoretical curve in Fig. 4. It is important to note that, at large volume fractions of filler, the CM rheology is strongly dependent on filler content. Materials poorly adapted to manufacture can also be obtained at low filler contents if the grain sizes are chosen improperly. Improper choice of grain sizes seems to be the reason for various failures in the manufacture of real propellants, particularly those within the range of the strong dependence $\mu(\phi/\phi_m)$ ($\mu_b = \text{const}$) close to $\phi/\phi_m = 0.60$ (see Fig. 4). The revealed law of viscosity increase with ratio ϕ/ϕ_m makes it possible to design propellants with a high volume fraction of filler by increasing ϕ_m .

Table 2 lists ϕ_m values calculated for different numbers of fractions of a spherical filler, the grain sizes of the fractions being essentially (approximately by an order of magnitude) different. It follows from these data that two (maximum four) grain sizes are sufficient to design a CM with sufficiently large volume fractions of disperse filler. The use of spherical particles improves the rheology of CM. If the grain sizes are essentially different, the fraction of the smallest particles uniformly distributed in polymer forms a sort of new binder with a certain μ_b . The optimization of ϕ_m is performed for a new set of fractions. In this case the number of fractions can be more than four.

The foregoing information, strictly speaking, is valid for compositions in which there are practically no physicochemical interactions of the particles with binder molecules or interparticle interactions. However, this is not the case with all materials. It is valid to say that the variety of rheological properties of CM with high filler concentrations is a result of the formation and destruction of coagulation structures. The main part of such a structure is a filler particle surrounded by the boundary layer of binder whose properties differ from those of the bulk binder due to the effect of particle surface. The structure formation can be controlled by the addition of SAS, which, spreading over the particle surface, reduces the thickness and changes the adsorption layer properties. To gain the highest effect, it is very important to apply SAS to proper

filler fractions. By itself, the addition of SAS allows the reduction of viscosity by two orders of magnitude.

The structures can also be destroyed mechanically. At present, this method is practiced widely. There are processes wherein compositions are not subject to external effects (free casting), techniques involving moderate external effects (injection molding), and processes conducted under high pressures (extrusion molding).

Mathematical description of production processes for particular compositions includes a complex system of differential equations in terms of partial derivatives, based on conservation laws and the rheological Fourier law of thermal conductivity. Taking into account the features peculiar to the equipment, processes, and certain constructions, the limiting conditions for temperature, time, and pressure are formu-

Table 2 Maximum volume fraction of filler vs number of fractions

| Number of fractions | ϕ_m |
|---------------------|----------|
| 1 | 0.7405 |
| 2 | 0.9326 |
| 3 | 0.9825 |
| 5 | 0.9988 |
| 10 | 0.9999 |

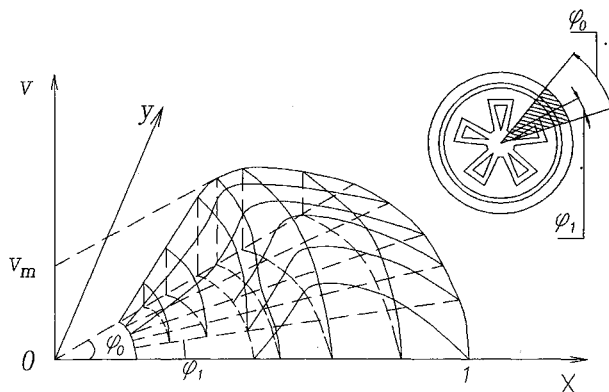


Fig. 5 Diagram of velocity distribution for a steady-state flow in a press-form with a central body.

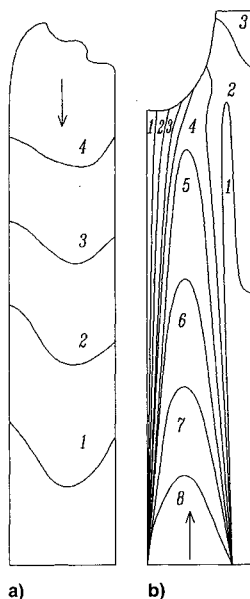


Fig. 6 Distribution of successive portions of uncured propellant in units filled by a) cast molding and b) extrusive casting.

lated. Mathematical models have been developed for the main stages of production of composite SP. A computer code has been created for the technological design. The code provides the choice of component ratios and regimes of mixing and feeding the CM form mixers, calculation of hydrodynamic resistances of equipment units, calculation of viscous flow in press-forms of various configurations (Fig. 5), determination of the topography of the final distribution of material portions in the case volume taking into account the variations in rheology, density, and production rate (Fig. 6), and the minimization of temperature and time parameters for polymerization and cooling.

Mechanical Behavior of Polymers with High Content of Disperse Components

Complex studies of composite SP allowed us to reveal a number of general rules concerning the mechanisms of deformation and destruction of polymer-based composite materials.

At small strains ($\epsilon = 1-10\%$), the mechanical behavior of cured polymer systems loaded with disperse fillers depends mainly on the processes in the polymer (binder) itself. At stronger strains, the effects of adhesion at the polymer-filler interface are significant because the interface is particularly sensitive to changes in time, temperature, and humidity. Most materials under study manifest enhanced stiffness at the initial steps of deformation ($\epsilon = 0-2\%$). This is associated with the presence of unstable initial frame structures that disappear irreversibly under mechanical preloading (Fig. 7). The effect of permanent memory and its attendant deformation anisotropy can cause the anisotropy of the properties within different zones of construction units that usually experience non-uniform stresses.

The deformation mechanisms of filled polymers depend to a large extent on the rheological character and physical nonlinearity of the material characteristics. The temporal behavior of the mechanical properties depends on the type of binder, and manifests itself as a creep, relaxation, and a dependence of properties on the rate of stress application. The physical nonlinearity of polymeric systems with disperse fillers is associated with the nonlinear behavior of the binder and its structural changes under deformation, as well as with void formation around filler particles. Depending on the contri-

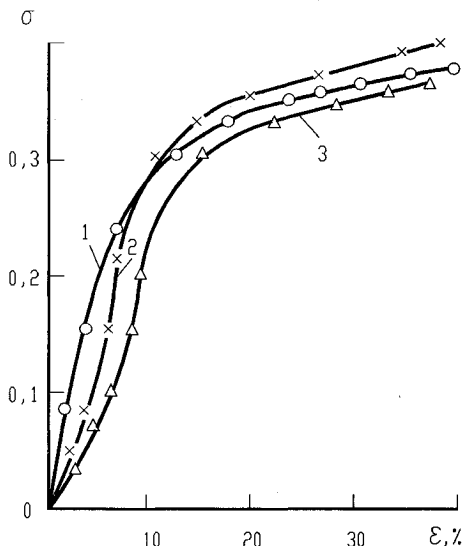


Fig. 7 Effects of physical nonlinearity and permanent memory in a preloaded propellant subjected to tension at the rate $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$: 1, initial material; 2, static preloading ($\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$ up to $\epsilon = 10\%$); 3, vibrational preloading [$\sigma = 0.15 + 0.08 \cdot \sin(\omega t)$, MPa, $f = 3 \text{ Hz}$, $t = 3h$].

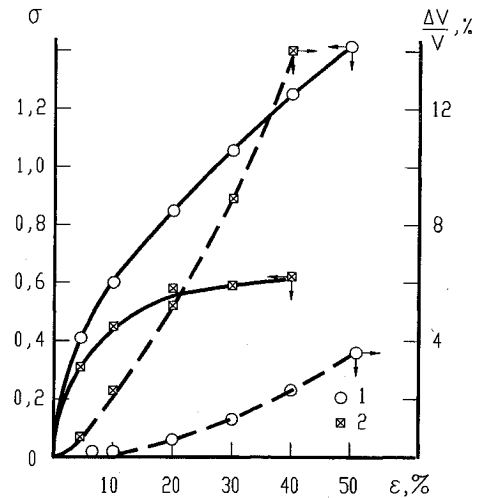


Fig. 8 Effect of hydrostatic pressure on tensile stress σ , MPa (solid line) and volume changes $\Delta V/V$ (dashes) for composite SP under tension ($\dot{\epsilon} = 10 \text{ s}^{-1}$): 1, $p = 0.1 \text{ MPa}$; 2, $p = 4 \text{ MPa}$.

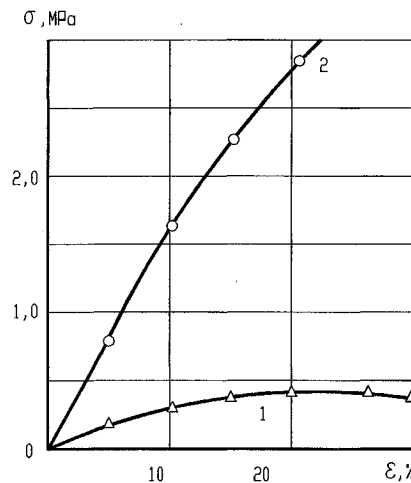


Fig. 9 Dependence of SP tensile stress at different rates of loading and hydrostatic pressures: 1, $\epsilon = 10^{-3} \text{ s}^{-1}$, $p = 10 \text{ MPa}$.

bution of these factors, the linear deformation range for different compositions can be rather wide (1–30%).

Structural changes and formation of microvoids can be reduced by applying external hydrostatic pressure, which essentially diminishes the development of volume changes during deformation and extends the linearity range of mechanical properties of composite SP (Fig. 8). Typically, the material strength increases 2–3-fold. For compositions exhibiting essential changes in volume under deformation and for gas-containing materials, the application of hydrostatic pressure can increase the limiting strength value by a factor of 8–10 due to retardation of structure degradation (Fig. 9).

Microstructural investigations show that in composite SP with optimum component ratio, filler particles are coated with a thin and firmly bonded layer of binder. Fractures of such samples exhibit no pure crystals. Tension leads to microruptures first in the vicinity of large filler inclusions within thin binder layers. The concentration of microdefects larger than $10 \mu\text{m}$ is relatively low (approximately $7 \times 10^3/\text{cm}^3$), and their contribution to volume changes of the material, which precede the destruction, is insignificant (approximately 2.5%). Microdefects with sizes less than $10 \mu\text{m}$ and concentration $c \approx 10^8/\text{cm}^3$ have a significant effect on volumetric changes before material failure [$(\Delta V/V)_{\text{max}} \approx 5-20\%$]. The number of microdefects coincides with the number of filler particles in order of magnitude.

Microvoids appear at the initial stages of deformation and their volume almost linearly depends on the deformation value. Mathematical estimations have shown that the contribution of microdefects in increasing extreme deformation and decreasing lateral deformation of samples subjected to axial tension can reach 20%. For systems based on butyl rubber, the stronger extreme deformation under lower temperature and deformation rate is to a large extent (up to 60%) due to the increased contribution of microvoids. However, the effects of material weakening under increasing loading (non-linearity), as well as the effects of material softening after preliminary loading, cannot be accounted for only by deformation-induced microdefects. The changes in material properties described above can also be due to modifications in the initial structure of binder that are not accompanied by volume changes of any significance. The production of certain units using filled polymeric materials shows that the mechanical properties and their distribution in a real construction depend essentially on the formula of composite SP and on technological factors. For example, the material deformability is lower at the propellant-press-form interface. In cast dumbbell-like samples (effective diameter of test section 20 mm) of butyl-rubber-based composite SP, the extreme deformations are 1.5–1.6 times less than those in paddle-shaped samples (cross section 7.5×7.5 mm) composed of the same dumbbells. The destruction starts from the outer surface of a dumbbell. In the zones where the samples are in contact with other parts of the construction, the stiffness and limit tension characteristics of composite SP change, causing significant changes (3–10-fold in the deformation modulus and 1.2–1.8-fold in tensile strength) in the mechanical properties of the material.

In practice, for optimization of filled polymeric compositions, mathematical models are used that include the regression dependence of mechanical properties on the content of the main components, as well as the physical parameters that characterize the influence of filler on the mechanical behavior of composite SP:

$$[A] = \sum_i [(a_i + b_i X_i)^{n_i} \cdot f(w)] \quad (6)$$

The state equations describing deformation of the systems under study, are as a rule formulated in the form of relations between deviators and spherical tensors of stresses and strains. The mathematical model most generally employed is a version of the nonlinear theory of hereditary viscoelasticity. To formulate the destruction mechanisms of composite SP, a matter of principle is the experimental discovery of the weak influence of the prehistory of loading on the limit mechanical characteristics, which in most cases are determined by final loading. Only very strong preliminary loading (damages 0.6 and more) can lead to a change in the limit mechanical properties under the subsequent final loading. This fact allows one to estimate the reserve strength of constructions using the simplest deterministic criteria

$$\delta = [A] \prod_i K_i / \sum_i A_i \quad (7)$$

Stability of the Properties of Composite Materials

The problem of stability of the properties of composite materials is closely related to their practical application. No matter what the duty of a material energy source or structural material, the latter must usually keep its main qualities even longer than the storage and service life guarantee of the product.

The background of the stability of CM properties is based on studying the mechanisms and kinetics of possible chemical reactions: thermal decomposition of individual components,

interaction between the components, and secondary interaction of the products of the above reactions with initial compounds. Determination of rigorous temperature–time dependences of material behavior allows one to predict the storage life of a material, based on a given degree of admissible transformations. Control over the kinetics of various chemical reactions in composite materials makes it possible to govern their stability. It should be noted that even for present-day energetic CM, including advanced composite SP, in which oxidizing and reducing agents are in close contact, the optimum compositions have been designed that provide stability of the materials for up to tens of years.

The multicomponent nature of composite SP and their complex disperse state (they can simultaneously include true and colloid solutions, micro- and macrosuspended matters, cured polymers, etc.), determine the complexity and route of chemical reactions between components.

A study of the chemical compatibility of components has shown unambiguously that in most cases the chemical stability of a composition is determined by the entire ensemble of components and the state of aggregation of each component, and that it cannot be derived from data on the compatibility of the components in binary, triple, etc., mixtures.

In real compositions, a number of serial-parallel homogeneous and heterogeneous reactions occur that cannot take place in the simple mixtures of individual components. To gain chemical stability of propellant formulations one must enhance or retard these reactions by special additives or by structural–physical means, since the rate and direction of chemical processes in composite SP depend substantially on the reactivity of compounds. A possible scheme of chemical interactions for a composite SP is shown in Fig. 10.

However, chemical processes do not exhaust the problems of CM stability. The application of highly plasticized polymers as binders calls for investigation of phase stability and estimation of free energy variations within certain ranges of temperatures and external loading at which the plasticizer cannot pass into the individual state. Account must be taken of changes in the polymer state during formation of three-dimensional

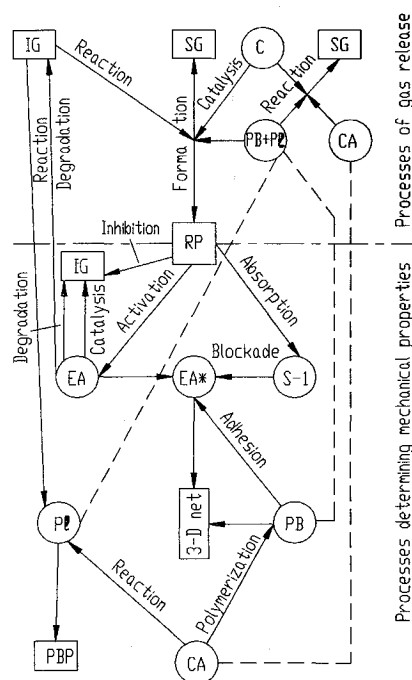


Fig. 10 Scheme of chemical interactions in composite SP. Components (circles): BP, polymer B; PI, plasticizer; CA, curative agent; S-1, stabilizing additive; EA, energetic additive (EA*, activated EA); C, catalyst. Reaction products (squares): SG, soluble gases; IG, insoluble gases; RP, reaction products; and PBP, plasticized polymer.

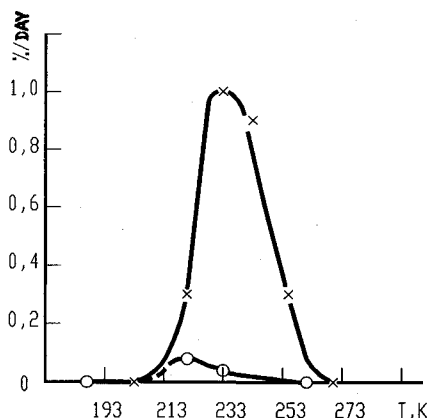


Fig. 11 Temperature dependence of crystallization rate (% per day) for nonplasticized (x) and plasticized (o) butyl rubber in a composite propellant.

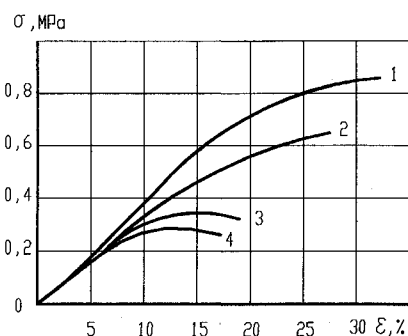


Fig. 12 SP strength vs deformation depending on the amount of absorbed moisture: 1, virgin material; 2, 0.019%; 3, 0.030%; 4, 0.034%.

structures in the inherent volume of the polymeric matrix and in the layers adherent to the filler crystal surface due to reaction with curing agents.

Complex investigations have shown that the lower limit for the percentage of a polymer with a reproducible regular three-dimensional net, which provides desired mechanical characteristics of CM, ranges between 12–15%. Further reduction of the polymer content, which is sometimes profitable (e.g., for increasing composite SP energetics), requires a special design to compensate for the insufficient mechanical characteristics of the polymer.

The polymer component is employed in its high-elasticity state, which makes CM resistant to dynamic loading. However, polymers can pass to the crystalline state. Therefore, in designing composite SPs and other CMs it is important to know the aggregate state of a certain binder. It has been established that many elastoplastics can be transferred to the crystalline state. In this process, the role of molecular structure is very important. The introduction of a plasticizer reduces the rate of transition to the crystalline state. The crystallization rate passes through its maximum as T changes (Fig. 11).

The change in the phase-state of polymer affects the mechanical parameters of CM, which is unacceptable during its working life. This detrimental effect can be eliminated by modification of the available and purposive synthesis of new elastomers. The change of the state of CM and the instability of mechanical characteristics in the general case and of ballistic parameters in the particular case of composite SP are conditioned by diffusion transfer of individual components. Such processes occur in the case in which concentrations of individual components at interfaces are different. A detailed study of the phenomenon has shown that the diffusion of

plasticizers or additives into the material of the mold or technological instrument during the manufacture of SP charges leads to the formation of surface layers of CM ("crusts") with other properties. The diffusion of moisture into CM is a sufficiently common phenomenon and can cause, even at small concentrations, essential changes in the mechanical characteristics of the materials (Fig. 12).

It should also be emphasized that in reality certain CMs are subject to various types of radiation (from solar radiation to radiation from artificial high-energy sources), which also affect the CM characteristics. Many interesting theoretical and experimental results have been obtained in this field.

Conclusions

The invention, in the second half of the Twentieth Century, of a new class of energetic materials, SPs, became a significant achievement of scientific researchers that can be compared with the invention of black powder in the Seventh Century. This invention required solution of complex scientific and technological problems, and resulted in the creation of several powerful propulsion systems. In the original stages of the development of SPs, commercially available materials were employed as the components in propellant formulations. Specifically, AP was employed as the oxidizer and various binders were employed as the binder/fuel. Archival efforts regarding the creation of a fundamental basis for propellant design have led to the understanding of a mutual interaction between the physical and chemical characteristics of individual components, as well as for those of a propellant. It became obvious that the maximum energetic characteristics of a propellant could not be achieved without optimization of the parameters of every component, including their weight fraction in the formulation.

The continuing development of rockets and modern technical devices based upon the application of composite solid propellants to other needs raises problems concerning the formulation of propellants that can meet not only traditional, but also some new, requirements. Such development concerns, in particular, the enhancement of the storage of potential energy in solid propellants and the increase of rocket ballistic performance, the widening of the applications of such propellants and the variety of the available design solutions, and the improvement of the hazards and ecological safety of the systems that employ solid propellants. A database covering all aspects, e.g., oxidizers, binders, plasticizers, bonding agents, and combustion additives, of composite solid-propellant formulations has been developed at Altai, together with the understanding required to utilize this database to produce improved SPs.

With regard to the improvement of the ballistic performance, there are significant possibilities of the creation of new materials with unique properties. For instance, new oxidizers are being evaluated which have the potential for significant improvements in delivered performance, and chemists currently are involved with the synthesis of promising compounds containing polycyclic frameworks with strained atomic groups. These compounds have very low heats of formation and densities exceeding two g/cm³. Another possible approach for increasing ballistic performance is the improvement of the mechanical design, due to combining the optimal principles of liquid- and solid-propellant rocket motors, resulting in enhancement of the propellant mass fraction.

It appears realistic to assume that a combination of the achievements of the synthesis of new energetic materials and the creation of novel advanced propellant formulations, as well as achievements in the developments of new designs for propellant grains, may provide enhancements of solid-rocket specific impulse in the range of 40–45 lbf-s/lbm during the next decade.