EDN: XAVUHQ
УДК 681.5

Current State and Development of the Theory of Curing High-Energy Composite Polymer Materials

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Received 10.09.2023, received in revised form 29.10.2023, accepted 06.12.2023

Abstract. Within the framework of a two-component medium, based on a phenomenological approach, a system of governing equations has been developed that describes the thermomechanical behavior of an elastomer highly filled with fine particles under conditions of a curing reaction (vulcanization) with adhesive contact conditions at the filler-matrix interface. The model is intended to describe the stress-strain state in the temperature range covering the intervals of phase and relaxation transitions at finite deformations. The basic equations of thermo-mechano-chemistry turn out to be related to the mutual influence of the stress-strain state of the curing elastomer and reaction kinetics. The results of numerical experiments are presented that demonstrate the possibility of describing the characteristic features of deformation processes characteristic of highly filled elastomers during curing.

Keywords: cure, high-filled polymer, finite element method, curing resudual stress, viscoelasticity, chemical shrinkage.

Citation: K.A. Chekhonin, Current State and Development of the Theory of Curing High-Energy Composite Polymer Materials, J. Sib. Fed. Univ. Math. Phys., 2024, 17(1), 106–114. EDN: XAVUHQ.

Solid propellants, due to their high energy density, high specific impulse, safety, long shelf life, easy operation, and low cost, are extensively used in rocketry systems to deliver the required thrust to rockets or missiles. Solid propellants are usually made of an elastomer highly filled with well-dispersed micrometric oxidizer and metal particles (up to 90% volume fraction). These materials can be engineered to meet a set of requirements. This translates into a balance between combustion, processing and mechanical properties. Hydroxyl-terminated polybutadiene (HTPB) propellant with nitrate additives represents a significant breakthrough in high-energy solid propellants in solid rocket motors (SRMs). In the preparation of the HTPB propellant grain, the propellant slurry needs to be cast and cured separately at an elevated temperature for the required number of days and then cooled to the room temperature before storage. During the curing process, several phenomena, such as chemical shrinkage, thermal expansion, and differences in the thermal expansion coefficient of materials, can lead to the generation and development of residual stress in the propellant grain, and then a reduction in the mechanical properties of the propellant materials, which is even large enough to crack the propellant grain without mechanical loading. Therefore, it is important to evaluate the stresses and strains of the propellant grain in the manufacturing process. In general, residual stresses and strains in a propellant grain of case-bonded SRM are primarily generated by effects [1–8]: Level of content, size,

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shape and thermomechanical properties of filler particles; Thermal expansion and contraction during the curing process; Chemical shrinkage of the propellant during the curing process; Different thermal expansion coefficients between propellant, technological needle and case; Difference between curing temperature and operating temperature of SRMs.

For composite materials such as composite solid propellant, the overall residual stress introduced from curing in previous studies was mainly determined by considering two contributions: the thermal expansion and contraction of propellant cooling from the curing temperature to room temperature and the chemical shrinkage of binder resin from the crosslink polymerization during curing [4]. It was found that thermal expansion and contraction during the curing and cooling down processes was the most significant factor in the generation of residual stresses [5]. However, chemical shrinkage cannot be neglected; the research shows that the residual stresses due to chemical shrinkage may contribute up to 33% of the total residual stresses in composites [5]. Works devoted to the study of stress evolution during propellant grain cure are extremely rare in the available literature. The effect of chemical shrinkage on residual stresses in propellant grain is usually converted into a temperature effect. For composite solid propellant, the conversion temperature is usually 8–10 °C [5].

In the curing process, the crosslinking reaction of the binder system is induced between a prepolymer and curing agent. The final crosslinking structures present some new bonds and the molecular growth continues over time until a perceptible gel-like lump can be formed; this also resulted in volume shrinkage of the binder system [1, 5]. The point at which the binder system is converted from the liquid phase to the solid phase is called the gel point [1]. Typically, most propellants the degree of cure level at the gel point is low ($< 0{,}1$) begin to shrink. The modulus of the propellant increases rapidly after the gel point and there is still some volume shrinkage, since the residual stress level mainly depends upon the product of the volumetric shrinkage and the stiffness of the propellant material [5], and a considerable residual stress will be introduced. The curing shrinkage stress should be paid enough attention in the residual stress analysis of the propellant grain.

The work [4] proposed a three-dimensional model of the cure of propellants in solid rocket motors in a geometrically linear viscoelastic formulation. The theoretical model is based on Hermann's variational principle using the temperature-polymerization-time analogy. The influence of temperature regimes of curing and contact conditions with the central profile body forming the combustion channel on the evolution of technological stresses is shown. In [8], an algorithm was proposed for optimizing curing temperature conditions, which makes it possible to reduce the gradients of temperature and conversion fields, and, consequently, the level of technological stresses. The model was further developed in [9–12], taking into account compression pressure during solidification, contact conditions of friction-sliding and peeling with the central profile body forming the combustion channel. Works [10] are devoted to the development of geometrically physically nonlinear constitutive relations under the conditions of the binder curing reaction. Thermodynamically consistent constitutive relations based on the hybrid potential of deformation energy are proposed, taking into account the incompressible properties of the elastomer binder, their geometric and physical nonlinearity, the tension-compression asymmetry in mechanical property propellant, taking into account the influence of the stress level on the kinetics of the curing reaction, as well as changes in Poisson's ratio and compression pressure during the curing process.

The determining influence on the evolution of technological stresses and the final physical, mechanical and functional properties of solid propellant is exerted by its microstructure. What-

ever the property considered, the size of the particles has been identified as a critical material parameter, with opposite effects on the different phenomena. A compromise is commonly reached by using polydisperse granulometries of particles. From a mechanical view point, have demonstrated the influence of the size, shapes particles and adhesion properties between particles and binder during curing. Moreover, it plays a key role in shaping the future properties of solid propellant. Therefore, the stress and strain of an HTPB propellant grain during the entire curing and cooling processes was multiscale investigated in this paper. The organization of the paper is as follows. The theoretical framework for analyzing the residual stress and strain of the HTPB propellant is constructed in Section 1. The finite element modeling of the numerical simulation the residual stress and strain in the HTPB propellant grain is analyzed in Section 2. The multiscale modeling in the located inner bore-free surface of the propellant grain is analysed in Section 3. Finally, the conclusions are summarized in Section 4.

1. Theoretical models

The thermo-chemical model is composed of heat conduction and cure kinetics. The temperature field of the propellant grain depends on the external curing temperature profile and the heat released by the curing reaction of the propellant, which is considered as a non-linear temperature transfer problem with a heat source. Due to limitations in the volume of the article, the defining relationships for solid propellant cure are taken from the work [10] and are not presented here.

The major structural components of the solid rocket motor (Fig. 1) considered in this work are made of a fiberglass reinforced plastic (FRP) composite case, Ethylene propylene diene monomer (EPDM) insulation, Hydroxyl-terminated polybutadiene (HTPB) based propellant grain and liner [7]. Aluminum bosses are located at the rear port of the motor. The FRP case and aluminum bosses are modeled as linear-elastic. Their elasticity modulus E, Poisson's ratio v, thermal expansion coefficient α are from reference [7].

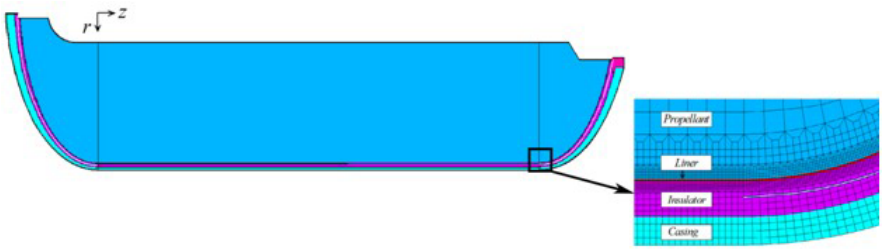

Fig. 1. Geometry model and detailed view of local mesh of solid rocket motor

The EPDM insulation has good hyperelastic properties, and it is modeled with a Moony–Rivlin strain energy potential:

$$U = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) + (J^{el} - 1)^2/D_1,$$

where U is the strain energy potential, I_1, I_2 are the first and second deviatoric strain invariants, respectively. J^{el} is the elastic volume ratio. D_1 is material incompressibility parameter. C_{10}, C_{01} are material constants. Poisson's ratio vis assumed to be 0.495, and thermal expansion coefficient (CTE) is assumed to be $1.8 \times 10^{-4}\,^{\circ}C$ [7].

The incremental stress and strain in the first step are calculated as:

$$\sigma = \sum_{i=1}^{N} \{\Delta\sigma\}_i = \sum_{i=1}^{N} \{C\}_i \{\Delta\varepsilon\}_i$$

where N is a specified incremental time step, $\Delta\sigma_i$ and $\Delta\varepsilon_i$ are the stress and strain at each time step i, and C is the stiffness matrix of the propellant.

In the second step, the general form of the integral constitutive equation for the three-dimensional viscoelastic materials is as follows:

$$\sigma_i(t) = \int_0^t C_{ij}(t - t') \frac{\partial \varepsilon_j}{\partial t'} \, dt' \tag{1}$$

where σ_i and ε_i denote the stress tensor and Henky's strain vectors, respectively. C_{ij} is the relaxed stiffness matrix. t and t', respectively, represent the current time and dummy time integration variable. Equation (1) is applicable to isothermal conditions. For a liner orthotropic viscoelastic constitutive law under the curing process or changeable temperature where the material stiffness varies with the temperature and degree of cure, it can be expressed in the following form with the time-temperature equivalence principle [4]:

$$\sigma_i(t) = \int_0^t C_{ij}(\zeta - \zeta') \frac{\partial \varepsilon_j}{\partial \tau} d\tau$$

where ζ and ζ' are the current and past reduced time, respectively. They are the function of the degree of cure α and temperature T, and are given by:

$$\begin{cases} \zeta(t) = \displaystyle\int_0^t \frac{d\tau}{a_T[\alpha_{ref}, T(\tau)]} \\ \zeta'(\tau) = \displaystyle\int_0^{t'} \frac{d\tau}{a_T[\alpha_{ref}, T(\tau)]}, \end{cases}$$

where a_T is displacement conversion factor, which can be described by the following WLF equation:

$$\lg a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)}$$

where $C_1(\alpha)$ and $C_2(\alpha)$ are material constants [1], which can be determined by experiment, T is the current moment temperature, and T_r is the reference temperature.

2. Finite element modeling

The curing and cooling behavior of the propellant was simulated using a sequentially coupled formulation based on the FIDESYS software platform [13] with additional use of home code in the form of a subroutine. Firstly, the thermal chemical model was used to simulate the heat generation and heat transfer process of the propellant grain during curing and cooling, and the temperature and curing degree of each node were obtained. Then, the thermal mechanical model was introduced to investigate the residual stress and strain of the propellant grain.The curing kinetic parameters of the HTPB propellant adopted in this paper are provided in Ref. [4]. To check the accuracy of the simulation method in this paper, the FEM simulation result of curing process was compared with the result performed [14], which is based on the numerical method of

finite volume. The numerical solution specifications were exactly the same as the conditions in Ref. [14]. Fig. 2 compares the cure degree in the center of three-dimensional modeling adopted in the Ref. [14]. It is clear that the results of the cure degree obtained by the two methods are in good agreement and support that the numerical method in this paper reasonably well captures the curing characteristics of the propellant.

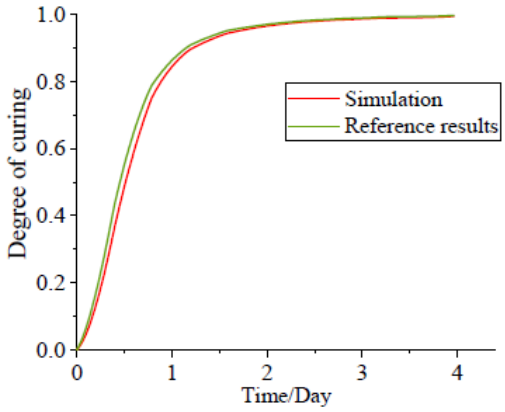

Fig. 2. Comparison of the cure degree between the simulation and the result of Ref. [14]

Fig. 3 presents the temperature of the HTPB propellant grain cured at 60°C for 24 h, 72 h, and 160 h. It can be seen that the temperature in the center of the propellant grain is higher

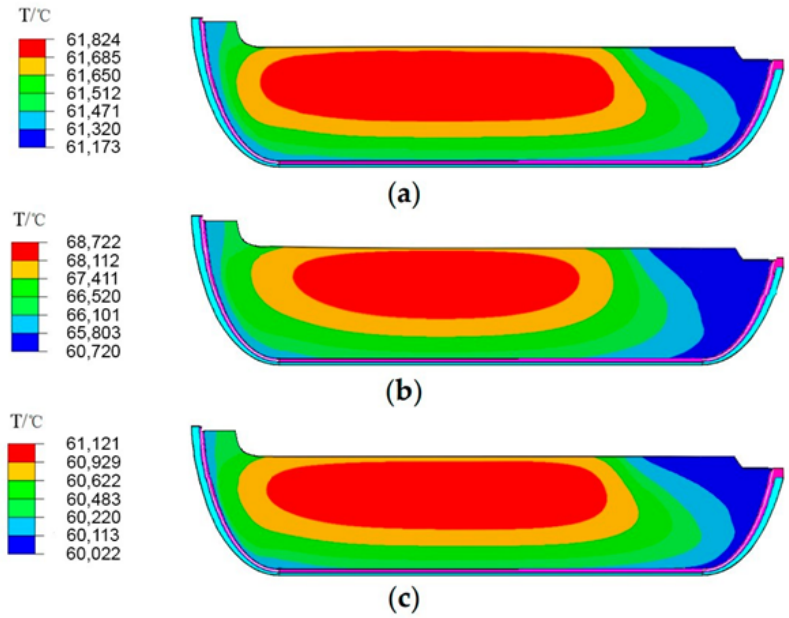

Fig. 3. Contours of the temperature: (a) 24 h, (b) 72 h, (c) 160 h

than that in the periphery during the curing process. The temperature in the grain also tends to

be uniform at the end of curing (160 h). Fig. 4 depicts the curing degree of the HTPB propellant grain cured at 60°C for 24 h, 72 h, and 160 h. It can be seen that the curing degree show the same distribution trends as temperature. The curing degree in the center of the propellant grain is higher than that in the periphery. At the end of curing, the curing degree in the interior of the grain tends to be uniform, reaching above 0.98.

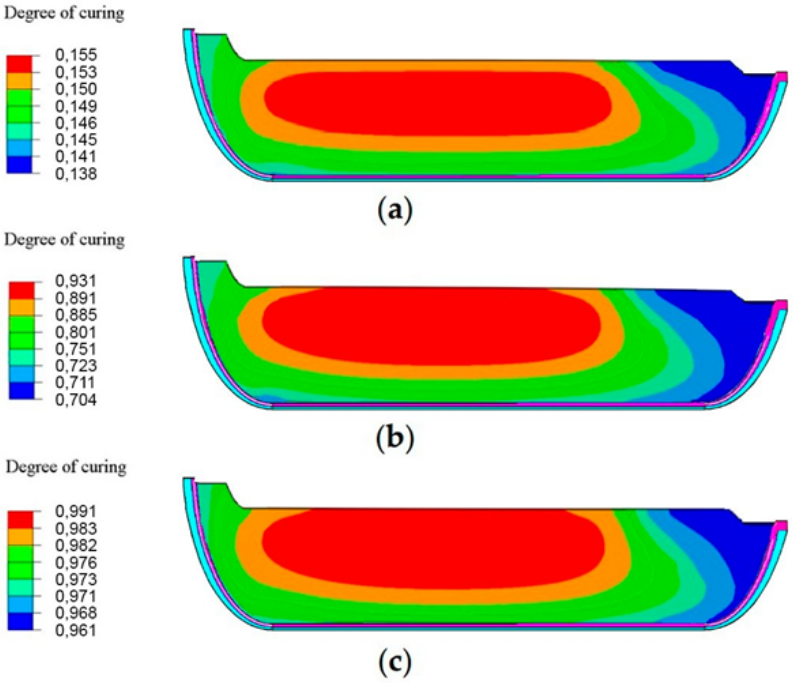

Fig. 4. Contours of the cure degree: (a) 24 h, (b) 72 h, (c) 160 h

Equivalent stress and equivalent strain were adopted to characterize the evolution of process stresses and grain strains during the curing stage. From the results of numerical modeling it follows that the maximum equivalent stresses during the curing stage did not exceed the values are 24,4 KPa and 0,036, respectively. It is obvious that the maximum residual stress and residual strain are located at the inner bore-free surface of the propellant grain.

Fig. 5 presents the total residual stress σ_{tot} and total residual strain ε_{tot} grain after cooling down. It is obvious that the σ_{tot} and ε_{tot} were located inner bore-free surface of the propellant grain, and were 120 KPa and 0,103.

3. Multiscale modeling

During multiscale modeling in the located inner bore-free surface of the propellant grain (for the meso-dimensional scale this is a node of the finite element mesh), we form a database of initial and time-varying data on the degree of cure, temperature and strain tensor components, which are initial and boundary conditions when considering the evolution of the stress-strain state in a representative volume of the curing composite. Fig. 6, a shows a representative volume of propellant of size $L = 0.582$ mm using an adapted finite element mesh (step $h = L/40$). Its size was obtained by varying it based on the conditions of convergence of volume-averaged finite

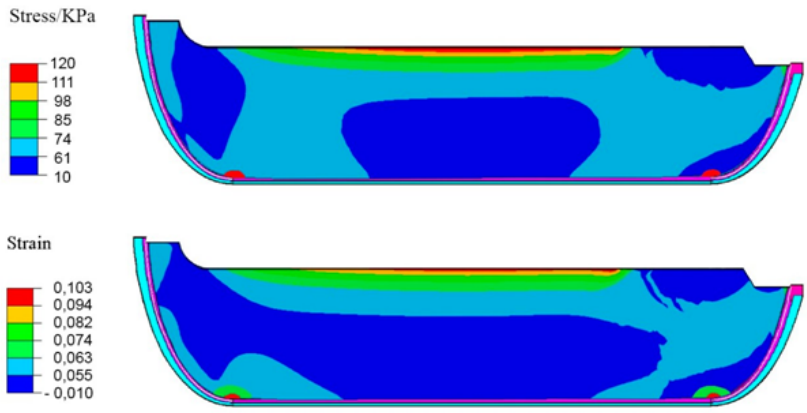

Fig. 5. Contours of the principal stress (a) and principal strain (b) during the cooling process

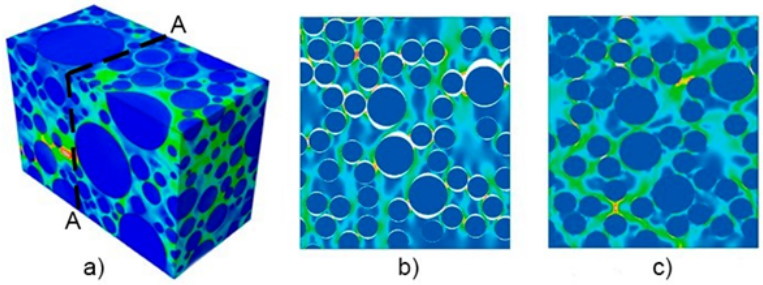

Fig. 6. Evolution of a bidisperse random cell submitted to curing shrinkage stress(a) Initial volume microstructure, (b) early damage occurring primarily around large particles without adhesive in section A-A and c) with adhesive at the end of the curing stage

stress element. At the boundary between filler particles and the curable binder, we establish adhesion conditions [11], with a known change in the maximum dewetting stresses and the relative movement of the contacting surfaces in functional dependence on the degree of curing and the type of adhesive [11]. When the filler particles separate from the curable binder at the free boundaries, we establish Signorini's boundary conditions with friction [4]. Fig. 6 shows the results of calculations of the evolution of the propellant microstructure without adhesive and with adhesive at the end of the curing stage. Consequently, the correct choice of the type of adhesive and the level of compression pressure during the curing process has a significant impact on the detachment of particles from the binder, the development of porosity in the propellant and the formation of micro-cracks up to the main ones.

Conclusions

The residual stress and residual strain of the HTPB propellant grain during the curing and cooling down process was investigated through numerical simulation. The conclusions are as follows:

1. There is a temperature gradient in the HTBP propellant grain during the curing at 60°C. The maximum temperature difference is about 9°C and the maximum temperature is located

on center of propellant grain. At the end of curing, the temperature in the interior of the grain tends to be uniform. The curing degree in the HTPB propellant grain during the curing process has the same trend as temperature.

2. The residual stress/strain of the HTPB propellant grain during the curing and cooling down process are mainly composed of curing shrinkage stress/strain in the curing process and thermal stress/strain in the cooling process. The curing shrinkage stress and strain in the curing process account for 22% and 35% of the whole process, respectively.

3. The stress and strain of an HTPB propellant grain during the entire curing processes was multiscale investigated. The correct choice of the type of adhesive and the level of compression pressure during the curing process has a significant impact on the dewetting of particles from the binder, the development of porosity in the grain and the formation of micro-cracks up to the main ones.

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Современное состояние и развитие теории отверждения высокоэнергетических полимерных материалов

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Аннотация. В рамках двухкомпонентной среды на основе феноменологического подхода разработана система определяющих уравнений, описывающих термомеханическое поведение высоконаполненного мелкодисперсными частицами эластомера в условиях протекания реакции отверждения (вулканизации) с адгезионными контактными условиями на границе наполнитель — матрица. Модель предназначена для описания напряженно-деформированного состояния в температурном диапазоне, охватывающем интервалы реализации фазовых и релаксационных переходов при конечных деформациях. Основные уравнения термо-механо-химии оказываются связанными с взаимным влиянием напряженно-деформированного состояния отверждаемого эластомера и кинетики реакции. Приведены результаты численных экспериментов, демонстрирующих возможность описания характерных особенностей деформационных процессов, свойственных высоконаполненным эластомерам при отверждении.

Ключевые слова: отверждение, высоконаполненный полимер, метод конечных элементов, остаточные напряжения при отверждении, вязкоупругость, химическая усадка.