International Journal of Solids and Structures 51 (2014) 2019–2026

Contents lists available at ScienceDirect

International Journal of Solids and Structures

journal homepage: www.elsevier.com/locate/ijsolstr

Mechanical properties of propellant composite materials reinforced with ammonium perchlorate particles

P.A. Kakavas *,[1]

Technological Educational Institute of Western Greece, M. Alexandrou 1, 26334 Patras, Greece

ARTICLE INFO

Article history:
Received 10 May 2013
Received in revised form 29 January 2014
Available online 26 February 2014

Keywords:
Ammonium perchlorate particles
Rubber materials
Glass beads
Foam materials
Propellant composites
Creep and relaxation
Strain energy density

ABSTRACT

The purpose of this article is the theoretical interpretation of the experimental data on a continuum Neoprene binder, a glass bead-filled polyurethane binder, and unbound micropulverized ammonium perchlorate particles. After conducting stress relaxation and creep experiments, it is concluded that the large deformation behavior of the filled binder can be described in part in terms of the large deformation behavior of the continuum binder. The time scale of relaxation of stress in the filled binder is much longer than that of the unfilled binder. This has been determined by frictional processes which took place between the filler and the binder as well as among the filler particles. As a result of relaxation and creep studies on ammonium perchlorate (AP) particles, it has been found that the time scale of relaxation is of the same order of magnitude as that of the filler binder. In addition, it is believed that the static indeterminacy of the unbound particles helps to explain much of the strain variation at given stress level that is observed in tensile experiments of composite propellants.

1. Introduction

Composite propellants made of solid oxidizer such as ammonium perchlorate or ammonium nitrate, a rubber such as HTPB or PBAN (may be replaced by energetic polymers such as polyglycidyl nitrate or polyvinyl nitrate for extra energy), optional highly explosive fuels (again, for extra energy) such as RDX or nitroglycerin, and usually a powdered metal fuel such as aluminum. Ammonium perchlorate is an inorganic compound with the chemical formula NH_4ClO_4. It is also known as the salt of perchloric acid and ammonia. It is a powerful oxidizer, which is why its main use is in solid propellants.

There are four different types of solid propellant compositions (Vogt et al., 2002): (a) single based propellant that has nitrocellulose as its main explosive ingredient, where stabilizers and other additives are used to control the chemical stability and enhance the propellant's properties (b) double based propellant that consists of both nitrocellulose and nitroglycerin while other liquid organic nitrate explosives are added where the stabilizers and other additives are also used. Nitroglycerin reduces smoke but increases the energy output. Double based propellants are used in small arms, cannons, mortars and rockets (c) triple based propellant that consists of nitrocellulose, nitroquanidine, nitroglycerin and other liquid organic nitrate explosives. Triple based propellants are used in cannons (d) composites contain no nitrocellulose, nitroglycerin, nitroquanidine or any other organic nitrate. Composites usually consist of a fuel such as metallic aluminum, a binder similar to synthetic rubber and an oxidizer known as *ammonium perchlorate*. Composite propellants are used in large rocket motors. Ammonium perchlorate (AP) is produced by the reaction caused between ammonia and perchloric acid, and is the driver behind the industrial production of perchloric acid. It can also be prepared by the treatment of ammonium salts with sodium perchlorate. This process exploits the fact that the solubility of NH_4ClO_4 is about 10% of that for sodium perchlorate. Ammonium perchlorate crystallizes into colorless rhombohedra. The majority of ammonium perchlorate is used to make solid propellants. When the ammonium perchlorate is mixed with a fuel, like a powdered aluminum and/or an elastomeric binder, it can generate self-sustained combustion under atmospheric pressure. It is an important oxidizer with a decades-long history of use in solid rocket propellants space launch (including the Space Shuttle Solid Rocket Booster), military, amateur, and hobby high-powered rockets, as well as in some fireworks.

Landel (1961) was one of the pioneers to examine the viscoelastic properties of rubberlike composite propellants. Many materials

* Fax: +30 2610 434193.
E-mail address: Kakavas@teipat.gr

[1] This work has been carried out under the supervision of Professor Paul J. Blatz, along the graduate studies of the author at the University of Southern California. Professor Blatz passed away on May 10th 2010.

http://dx.doi.org/10.1016/j.ijsolstr.2014.02.015
0020-7683/

List of symbols

J_I	stretch invariants ($i = 1,2,3$)
λ_i	stretch ratio
t_i	principal true stress
σ_i	principal engineering stress
$W_i = \frac{\partial W}{\partial J_i}$	derivatives of strain energy function W, with respect to stretch invariants
μ	shear modulus of the material
μ_{nl}	nonlinear shear modulus of the material
f	material parameter
k	rate constant

of engineering importance have exhibited significant viscoelastic behavior in natural environments while been under mechanical loading of practical interest. An overview of the constitutive equations and models for fracture and strength of nonlinear viscoelastic solids was given by Schapery (2000). According to Schapery's paper the nonlinearities may be due to intrinsic, locally nonlinear stress–strain behavior that exists practically down to atomic or molecular scale, or may be due to the combined effect on macro-stress–strain equations of many defects that are large enough to be modeled using local continuum mechanics such as distributed micro-cracks or dislocations. Balzer et al. (2004) have investigated the effect of grain size on the high rate mechanical properties of an ammonium perchlorate (AP)/hydroxyl-terminated polybutadiene (HTPB) PBX. This PBX consisted of 66% AP and 33% HTPB by mass. The ammonium perchlorate was available in four different crystal sizes: 3, 8, 30, and 200–300 μm. Ho (2002) used a softening pre-multiplier to describe 1-D nonlinear viscoelastic response so as to study the response of solid propellants (e.g., HTPB/ammonium perchlorate) under high strain-rates ranging between 10^3 and 10^4 s^{-1}. Using rigorous homogenization theory for composite materials, Xu et al. (2008) have proposed a general 3-D nonlinear macroscopic constitutive law, which models microstructural damage evolution upon straining through continuous void formation and growth. Nonlinear viscoelastic response of reinforced elastomers is modeled using a three-dimensional mixed finite element method with a nonlocal pressure field, which was studied by Areias and Matouš (2008). A general second-order unconditionally stable exponential integrator based on a diagonal Padé approximation was developed and the Bergström–Boyce nonlinear viscoelastic law (Bergström and Boyce, 1998) is now employed as a prototype model. An implicit finite element scheme with consistent linearization is used and the novel integrator is successfully implemented.

Sakovich (1995) has developed a computer-aimed approach for primarily optimization of propellant formulations. Possible ways of designing the advanced components of composite solid propellants (binders, plasticizers, curative agents, and oxidizers) were taken into consideration. Tussiwand et al. (2009) have studied an innovated set of fracture tests performed on a composite solid propellant based on ammonium perchlorate hydroxyl-terminated poly butadiene. An approach to simulate the motion of spherical and non-spherical fuel particles in combustion chambers was studied by Dziugys and Peters (2001). According to the work published by Dziugys and Peters (2001) viscoelastic contact forces include normal and tangential components with viscoelastic models for energy dissipation and friction. The method was applied to simulate the motion of spherical and elliptical particles in a rectangular enclosure, on a traveling grate and in a rotary kilm. Two approaches were applied to simulate the motion of the granular material (a) continuum mechanics and (b) discrete element. Theoretical and computational studies of viscoelastic solids are also well described (Simo and Hughes, 1998; Holzapfel, 2000).

In order to investigate the mechanical behavior of propellant materials one must understand the response of a continuum rubber material, since the binder in propellant solids is usually found in this type of medium. After that, one must examine (1) the response of a foam binder, when the oxidizer in propellant solids is placed in a highly foamed medium (2) also the response of a filled system when the propellant includes filler particles such as specifically ammonium perchlorate. Finally the response of a granular medium since the whole system is based on that medium. The analysis of the continuum binder will lead to the appropriate theory for the binder while considering it as a rubber-like solid which is the purpose for which the theory of rubber elasticity is used. Taking into account that the Blatz–Ko model is also used for this purpose the related constitutive equation is posed. The experimental data for an unfilled neoprene rubber material were analyzed in order to write the appropriate constitutive equation of this rubber material. By comparing the experimental data with the theoretical model one can compute the involved material parameters in the model. The experimental data were given based on three different temperatures: (a) At room temperature (b) below and (c) above this value. Experimental data were also posed for polyurethane foam filled with glass beads. The experimental data were fitted in with an appropriate theory of rubber elasticity. Relaxation data for a propellant material filled with ammonium perchlorate particles were also discussed and the data were fitted in agreement with Cole's distribution function for the same propellant solid. Creep data for the same propellant were also presented.

In the present article, the mechanical behavior of a propellant material reinforced with ammonium perchlorate particles was studied thoroughly. The theory of continuum binder is established in Section 2, where its response is contained in the strain energy function. In Section 3 the prediction of the mechanical behavior of foams in terms of the void content, hole size and rubber phase properties is described. In Section 4 the theory for filled binder is described while the generalized theory for granular solids that can be applied for the ammonium perchlorate particles is described in Section 5. Finally, we have decided to present some of the theory of soil mechanics, so as to help one to understand the nature of the forces that are developed between the particles.

2. Continuum binders

Modern composite propellants incorporate various thermoplastic and thermosetting resins or elastomers with a variety of nitrates or perchlorates as oxidizers. The most popular of the composite propellant systems in current use consist of ammonium perchlorate as the oxidizer and usually a copolymer or terpolymer of butadiene with other monomers such as acrylic acid or acrylonitrile as the binder. The analysis of this section will help one to completely understand the response of the binder to the propellant medium. This response is contained in the strain energy function W, which because of the principle of material indifference to rigid body motions in isotropic space, is an explicit function of the stretch invariants J_i (Blatz and Ko, 1962):

The constitutive equation derived from the function W, by the principle of virtual, is given by: