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MICROMECHANICS-BASED PREDICTION OF THERMOELASTIC PROPERTIES OF HIGH ENERGY MATERIALS

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ABSTRACT

High energy materials such as polymer bonded explosives are commonly used as propellants. These particulate composites contain explosive crystals suspended in a rubbery binder. However, the explosive nature of these materials limits the determination of their mechanical properties by experimental means. Therefore micromechanics-based methods for the determination of the effective thermoelastic properties of polymer bonded explosives are investigated in this research. Polymer bonded explosives are two-component particulate composites with high volume fractions of particles (volume fraction $> 90\%$) and high modulus contrast (ratio of Young's modulus of particles to binder of 5,000-10,000). Experimentally determined elastic moduli of one such material, PBX 9501, are used to validate the micromechanics methods examined in this research. The literature on micromechanics is reviewed; rigorous bounds on effective elastic properties and analytical methods for determining effective properties are investigated in the context of PBX 9501. Since detailed numerical simulations of PBXs are computationally expensive, simple numerical homogenization techniques have been sought. Two such techniques explored in this research are the Generalized Method of Cells and the Recursive Cell Method. Effective properties calculated using these methods have been compared with finite element analyses and experimental data.

Keywords: Micromechanics, thermoelastic properties, high energy materials, PBX 9501.

INTRODUCTION

Large scale simulations of the mechanical response of containers filled with high energy (HE) materials require knowledge of the mechanical properties of the materials involved. Though mechanical properties of HE materials can be determined experimentally, hazards associated with experiments on these materials, as well as the attending costs, make this option unattractive. As computational capabilities have grown and improved numerical techniques developed, numerical determination of the properties of HE materials has become possible. In this research, we explore micromechanics-based numerical methods for the determination of the mechanical properties of HE materials, specifically polymer bonded explosives (PBXs). The polymer bonded explosive PBX 9501 has been characterized experimentally and thus provides a basis for validating numerical calculations.

PBXs provide unique challenges for micromechanical modeling. These materials are viscoelastic particulate composites, contain high volume fractions of particles, and the modulus contrast between the particles and the binder is extremely high. For example, PBX 9501 contains about 92% by volume of particles and the modulus contrast between particles and binder

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of 20,000 at room temperature and low strain rates. In this research it is assumed that PBXs are two-component particulate composites with the particles perfectly bonded to the binder. The components of PBXs are assumed to be isotropic and linear elastic, and only the prediction of elastic moduli and coefficients of thermal expansion (CTEs) of PBXs is addressed. Finite element (FEM) analyses are used to compute the effective properties of PBX 9501 models and compared with properties computed using the Generalized Method of Cells (GMC). A new technique called the Recursive Cell Method (RCM) has been developed to address the limitations of GMC. Effective properties of PBX 9501 are also calculated using RCM for some microstructures simulating PBX 9501.

POLYMER BONDED EXPLOSIVES

Polymer bonded explosives are mixtures containing high volume fractions of stiff explosive crystals suspended in a continuous compliant binder. Some common PBXs (Gibbs and Popolato 1980) are shown in Table 1.

TABLE 1. Common polymer bonded explosives and their components.

PBX	Crystal	Weight (%)	Volume (%)	Binder	Weight (%)	Volume (%)
PBX 9501	HMX	95	92	Estane 5703 + BDNPA/F	5	8
PBX 9010	RDX	90	87	KEL-F-3700	10	13
PBX 9502	TATB	95	90	KEL-F-800	5	10

PBX 9501

PBX 9501 is a mixture of HMX particles coated by a binder composed of Estane and a plasticizer (BDNPA/F). The HMX crystals are in the stable β phase, have a monoclinic structure (Skidmore et al. 1997), and are linearly elastic at room temperature. The binder in PBX 9501 is viscoelastic. However at room temperature and low strain rates, the response of the binder is close to linear elastic. The composite (PBX 9501) is also linear elastic at room temperature and low strain rates. The elastic properties of PBX 9501 and it's components at 23^oC and a strain rate of 0.05/s (Gray III et al. 1998; Zaug 1998) are shown in Table 2.

TABLE 2. Elastic properties of PBX 9501, HMX and binder.

Material	Young's Modulus (GPa)	Poisson's Ratio	CTE ($\times 10^{-5}$/K)
PBX 9501	1.03	0.35	12
HMX	15.3	0.32	11.6
Binder	0.001	0.49	20

MICROMECHANICS METHODS

The term "micromechanics" describes a class of methods that use continuum mechanics for determining the effective material properties of composites given the material properties of the constituents. Methods of determining the effective elastic properties and coefficients of thermal expansion of particulate composites, containing up to 70% by volume of particles, are

well established (Hashin 1983; Markov 2000; Buryachenko 2001). Rigorous bounds on effective properties (Milton 2002) and various analytical methods for calculating effective properties (Torquato 2001) are also available. However, these techniques are not particularly useful for high volume fraction ($> 90\%$) and high modulus contrast composites such as PBX 9501. Therefore numerical techniques are essential to the solution of micromechanics problems for polymer bonded explosives.

Rigorous Bounds and Analytical Methods

Hashin-Shtrikman (Hashin and Shtrikman 1963) and third order (Milton 1981) bounds have been calculated for the effective elastic moduli of PBX 9501. The Rosen-Hashin bounds (Rosen and Hashin 1970) on the effective coefficient of thermal expansion of PBX 9501 have also been calculated. These bounds are shown in Table 3. The bounds on the elastic moduli are quite far apart and hence of no practical use. However, the bounds on the CTE are within 1% of each other.

TABLE 3. Bounds on the effective properties of PBX 9501.

	Expt.	Hashin-Shtrikman Bounds		Third Order Bounds	
		Upper	Lower	Upper	Lower
Bulk Modulus (GPa)	1.1	11.4	0.15	11.3	0.22
Shear Modulus (GPa)	0.4	5.3	0.01	5.0	0.07
CTE ($\times 10^{-5}$/K)	12	12.3	11.6	-	-

Analytical methods of interest for high volume fraction particulate composites include the composite spheres assemblage (Hashin 1962), the self-consistent scheme (SCS) (Berryman and Berge 1996), and the differential effective medium (DEM) approach (Markov 2000). Each of these methods makes simplifying assumptions about the microstructure of the composites. The CTE can be calculated given knowledge of the isotropic bulk modulus of the composite (Rosen and Hashin 1970). The effective elastic moduli of PBX 9501 calculated using SCS and DEM, and the corresponding CTEs are shown in Table 4. It can be observed that the analytical methods do not predict effective elastic moduli that are close to the experimental values. However, the predicted effective CTE is close enough to the experimental value to be of use and no further numerical calculation is required for this property.

TABLE 4. Effective properties of PBX 9501 from analytical models.

	Bulk Modulus (GPa)	Shear Modulus (GPa)	CTE ($\times 10^{-5}$/K)
Experiment	1.1	0.4	12
Self-Consistent Scheme	11.0	4.7	12.9
Differential Effective Medium	0.2	0.08	12.5

Numerical Approximations

The effective elastic moduli of a composite can be determined approximately by solving the governing differential equations using numerical methods. This process involves the determination of a Representative Volume Element (RVE), the choice of appropriate boundary

conditions and the solution of the resulting boundary value problem. The effective stiffness tensor (C^*_{ijkl}) of the composite is then calculated from the relation

$$\int_V \sigma_{ij}\, dV = C^*_{ijkl} \int_V \epsilon_{kl}\, dV \tag{1}$$

where V is the volume of the RVE, σ_{ij} are the stresses, and ϵ_{kl} are the strains.

Finite element analysis is the most commonly used numerical technique use to determine effective properties. The difficulties involved in discretization and solution of actual particulate geometries has led to simulations of simple geometries such as square or hexagonal particles, mostly in two dimensions. With improvement in computational capabilities random distributions of particles are being simulated more frequently (Mishnaevsky and Schmauder 2001). The large computational cost associated with finite element analyses and the poor accuracy in areas of high stress gradient have led to the exploration of alternative methods of calculating effective properties. Discrete spring network models (Day et al. 1992), integral equation based methods (Greengard and Helsing 1998) and Fourier transform based methods (Michel et al. 2001) show the most promise. However, a large amount of computation is still required for convergence in all these methods.

Generalized Method of Cells (GMC)

The Generalized Method of Cells (GMC) (Aboudi 1996) has been used to model the micromechanical behavior of various types of composites with relative success. The advantage of this method over other numerical techniques is that the full set of effective elastic properties can be calculated in one step. In this technique, the RVE is discretized into a number of subcells as shown in Figure 1. Continuity of displacements between subcells and subcell equilibrium are satisfied in an average sense using integrals over subcell boundaries. GMC has been shown to be more computationally efficient than finite elements for modeling fiber composites. A reformulated version of GMC (Pindera and Bednarcyk 1999) has been used for the calculations in this research.

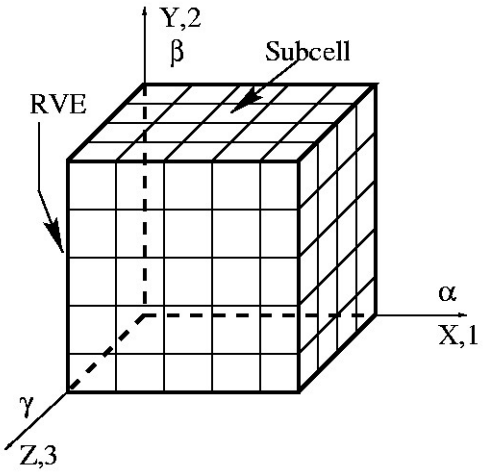

FIG. 1. Schematic of the Generalized Method of Cells.

Recursive Cell Method (RCM)

The GMC technique underestimates the effective properties of PBX 9501. The Recursive Cell Method (RCM) has been developed to provide a computationally efficient and accurate alternative to GMC. A schematic of RCM is shown in Figure 2. The RVE is discretized into subcells as in GMC. However, instead of calculating effective properties of the whole RVE in a single step, the effective properties of small blocks of subcells are determined at a time. The effective properties of the RVE are calculated by combining the effective properties of blocks using a recursive process. The effective properties of each block of subcells may be determined using any accurate numerical technique. We use a finite element based technique in this research. The RCM recursive scheme has been found to reduce the computational cost and remedy the shear-coupling problem of GMC.

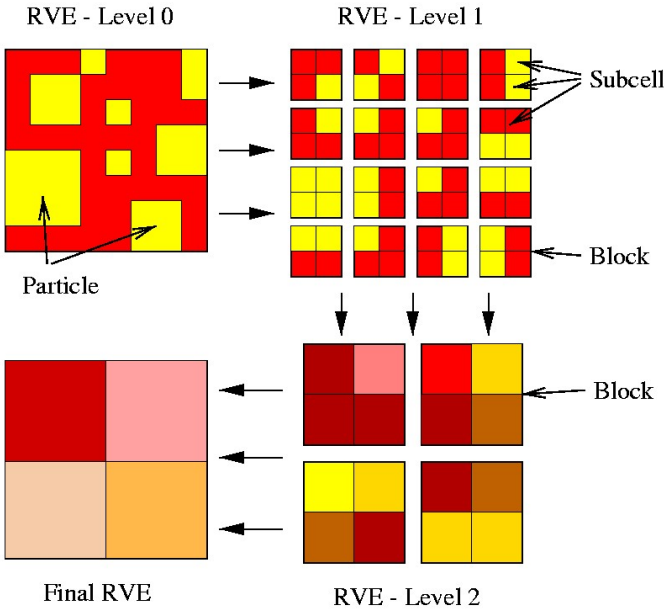

FIG. 2. Schematic of the Recursive Cell Method.

SIMULATION OF PBX 9501 MICROSTRUCTURE

Random sequential packing techniques were used to generate five different microstructures based on the particle size distribution in the dry blend of PBX 9501 (Skidmore et al. 1997). Each simulated microstructure contains around 100 particles that occupy approximately 87% of the volume of the square RVE, as shown in Figure 3. Since particles occupy 92% of the volume in PBX 9501, the binder is assumed to be "dirty", i.e., it contains 40% HMX particles by volume so that the total volume fraction of HMX in the composite is 92%. The effective properties of the dirty binder were calculated using the differential effective medium (DEM) approach.

The two-dimensional plane strain effective stress-strain relation for the composite is given by

$$\begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \tau_{12} \end{bmatrix} = \begin{bmatrix} C^*_{11} & C^*_{12} & 0 \\ C^*_{12} & C^*_{22} & 0 \\ 0 & 0 & C^*_{66} \end{bmatrix} \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \gamma_{12} \end{bmatrix} \tag{2}$$

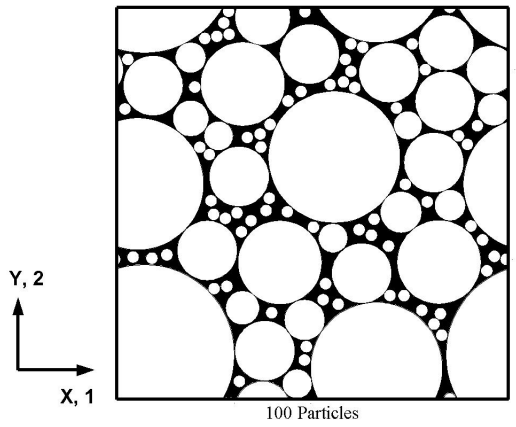

FIG. 3. Sample simulated PBX 9501 microstructure.

The effective stiffness matrix terms (C^*_{ij}) of the five PBX 9501 microstructures have been calculated using finite elements (FEM), GMC, and RCM. The average effective properties for the five microstructures and the corresponding standard deviations are shown in Table 5. On average, the five microstructures exhibit square symmetry. The FEM calculations (with 256×256 square elements) overestimate the effective normal stiffness (C^*_{11} and C^*_{22}) of PBX 9501 by around 15% to 25% on average. The corresponding effective stiffness matrix terms obtained by RCM (with 8×8 blocks, each containing 32×32 subcells) are around 60% higher than the FEM values and around two times the experimental values for PBX 9501. On the other hand, the values obtained from GMC form the normal stiffness terms are less than 1/10th the FEM and the experimental values. The FEM calculations underestimate the values of C^*_{12} for PBX 9501 by around 40%. RCM calculates the same average value of this component of the stiffness matrix as FEM. However, GMC predicts a much lower value that is around 1/7th of the stiffness of PBX 9501. The shear stiffness component (C^*_{66}) of PBX 9501 is calculated quite accurately by FEM and the error is only around 10%. RCM underestimates this stiffness component by around 60%. However, the value predicted by GMC is around 1/300 the experimental value and quite close to the Hashin-Shtrikman lower bound on the shear modulus.

TABLE 5. Effective stiffness of simulated PBX 9501 microstructures.

	C^*_{11} (GPa)	Std. Dev. (GPa)	C^*_{22} (GPa)	Std. Dev. (GPa)	C^*_{12} (GPa)	Std. Dev. (GPa)	C^*_{66} (GPa)	Std. Dev. (GPa)
PBX 9501	1.60		1.60		0.88		0.38	
FEM	2.03	0.81	1.85	0.51	0.54	0.20	0.51	0.34
RCM	3.20	0.96	2.99	0.50	0.54	0.27	0.27	0.16
GMC	0.15	0.02	0.15	0.02	0.12	0.01	0.01	0.001

DISCUSSION

The FEM calculations on the simulated PBX 9501 microstructures show that the mi-

crostructures are nearly isotropic. A better approximation of isotropy can be obtained if larger RVEs are modeled. The variability between models can also be reduced with larger RVEs. However, larger RVEs require larger meshes to model the increased degrees of freedom and hence are limited by computational cost. The FEM calculations are also found to predict values of stiffness that are slightly higher than the experimentally determined stiffness of PBX 9501. Three-dimensional calculations could lead to the prediction of lower stiffness for the PBX 9501 microstructures. In addition, the actual material contains voids and cracks that reduce the stiffness. The finite element calculations could incorporate interface elements to model interfacial debonds.

The RCM calculations can be performed at least three times faster than the full finite element calculations. Higher computational speeds can be obtained by reducing the number of subcells per block at each level of recursion though there is some loss in accuracy. Though the normal stiffness matrix components predicted by RCM are higher than those predicted by FEM, the values are quite acceptable considering the large modulus contrast between the components of PBX 9501. Additionally, the RCM calculations provide much better estimates of the effective properties than GMC, analytical models or rigorous bounds at relatively low computational cost.

The low effective normal stiffness predicted by GMC is because stress bridging effects are underestimated by this technique. The low shear stiffness is due to the lack of coupling between the normal and shear stresses and strains in GMC. Modifications of GMC that attempt to rectify these problems have been found to lose the computational efficiency of the original formulation.

CONCLUSION

The effective properties of the models of PBX 9501 are quite close to experimentally determined properties of PBX 9501. Therefore model RVEs using circular particles distributed according the particle distribution of a dry blend of PBX 9501 can be use to simulate PBX 9501. The RCM technique can be used to calculate effective properties of particulate composites quite accurately and at low computational cost. The technique is much faster than full FEM calculations using the same amount of discretization. Improved performance and accuracy can be obtained in RCM by proper choice of the number of subcells per block at each level of recursion. GMC is inadequate for calculating the effective properties of high energy materials because of the underestimation of stress bridging effects and the lack of coupling between normal and shear stresses and strains.

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