Piezoelectric response of energetic composites under an electrostatic excitation

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Piezoelectric response of energetic composites under an electrostatic excitation

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Ju Hwan (Jay) Shin¹ and Min Zhou¹,²,a)  

AFFILIATIONS  
¹The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0405, USA  
²School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0405, USA

a)Author to whom correspondence should be addressed: min.zhou@gatech.edu. Tel.: 404-894-3294. Fax: 404-894-8336

ABSTRACT  
Several high-explosive (HE) crystals are known to be piezoelectric. However, no systematic study has been carried out on how this effect can be utilized. In this paper, we report the results of an analysis on the response of composites consisting of HE crystals and a polymeric binder under electrostatic excitation. The HE crystals considered are 1,3,5-trinitroperhydro-1,3,5-triazine, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, pentaerythritol tetranitrate, and ammonium perchlorate. To explore avenues for enhancing the piezoelectric effect, the binder of the composites is taken to be piezoelectric polyvinylidene fluoride. The focus is on the distributions of induced electric field vector and mechanical stress in the microstructures. The effects of crystal–binder volume fraction, HE crystal size, and dielectric constants of the HE crystals are investigated. To further explore the effect, microparticles of lead zirconate titanate piezoelectric ceramic are introduced to some microstructures. For the HE crystals considered here, a coupled electromechanical analysis shows that the microstructural heterogeneities can enhance the local electric fields to as high as 1.34 times the applied $E$-field, causing the dielectric breakdown field strength of the overall composite to be much lower than the breakdown strengths of the constituents in the microstructure. In addition, the induced stress levels just prior to dielectric breakdown are well below the yield strengths of the respective constituents. As such, controlled dielectric breakdown, rather than mechanical damage, should primarily be used to facilitate hotspot formation, ignition, and chemical reaction. The likelihood of local dielectric breakdown within the HE crystals is systematically quantified as a function of applied electric field, microstructural attributes, and constituent behavior. To gauge the effect of the direct piezoelectric effect, one material case is also subjected to mechanical excitation in the form of compression. Under an applied external stress, the results show that the direct piezoelectric effect can lead to local yielding and thereby serve as a hotspot generation mechanism. On the other hand, the induced $E$-field is weak and unlikely to serve as a practical or efficient means of effecting hotspots within an energetic material. The analysis points out that simultaneous application of electrostatic excitation and mechanical excitation can also be considered.

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I. INTRODUCTION  
Following the early development and use of energetic materials (EMs), the research community has made concerted efforts to examine the ignition behaviors of high-explosive (HE) crystals used in propellants. For example, numerical and experimental analyses have been performed to understand the various material properties of energetic solids over a wide spectrum of size scales and to elucidate the underlying mechanisms that contribute to the ignition and detonation of an EM. In particular, one salient area of research has centered on analyzing the complex multiphysics behaviors, such as the coupled mechanical–thermal–chemical processes that EMs undergo when subjected to a dynamic impact. Of particular interest are the mechanisms and threshold conditions that lead to the initiation of chemical decomposition.

Apart from the mechanical input as a means to cause an ignition and reaction of an EM, there is a need to explore other mechanisms of excitation for actively manipulating the responses. In particular, piezoelectricity is one of the principal mechanisms used in energy harvesting and storage via active control. Furthermore, piezoelectricity has been shown as a viable method of facilitating ignition of EM through electromechanical sensitization and can be activated via both electric field and mechanical stress. Separately, electrical processes have received appreciable attention after static electricity was confirmed to be a possible source of accidental
reactions.\textsuperscript{32–37} For instance, Raha and Chhabra\textsuperscript{38} concluded that by mechanically shocking HE crystals beyond their detonation pressures, a sufficiently high electric field could be generated, leading to dielectric breakdown. The mechanism for dielectric breakdown can be explained as the ability of a strong electric field to pull the dielectric’s outer valence electrons away from its atoms. This eventually results in a substantially enhanced mobility of the bound charges and an increase in charge carriers, allowing for the conduction of electric current. Consequently, such localized discharge from EM crystals can engender transient Joule heating as energy is dissipated by the flow of electric current through the resistive medium. A more general question is: can the effects be systematically understood and utilized to develop propellants and explosives with tailorable ignition and reaction behavior?

In this study, the mechanical and electrical behaviors of piezoelectric energetic composites are investigated to understand their sensitivity to dielectric breakdown under an external electric field. The composites consist of a piezoelectric polyvinylidene fluoride (PVDF) binder and one of the several HE crystals, including 1,3,5-trinitroprohydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritol tetranitrate (PETN), and ammonium perchlorate (AP). While RDX, HMX, and PETN have been shown to be piezoelectric,\textsuperscript{29,38} AP is considered to be non-piezoelectric due to the centrosymmetric crystalline structure of its most commonly observed polymorph under ambient conditions. However, we note that non-centrosymmetric polymorphs of AP have also been predicted and observed.\textsuperscript{19,39,40} In the present analysis here, AP is assumed to be non-piezoelectric. Since it has been experimentally shown that lead zirconate titanate (PZT-5H) microparticles can be embedded in propellants,\textsuperscript{41} some analyses here include PZT-5H microparticles embedded in the PVDF binder to further enhance the piezoelectric effect. The microstructure configurations, with or without the PZT-5H microparticles, allow the effects to be systematically explored. While the focus is primarily on the response under electrostatic excitation, one set of calculations is also carried out to gauge the response under mechanical excitation as well.

The analyses capture the coupled dielectric and piezoelectric\textsuperscript{32–37} effects. The effects of microstructural heterogeneities, HE crystal volume fraction, size distribution, and permittivity are evaluated based on the peak electric field in the composites. The results are then quantified statistically using a probability density function (PDF) to enable the understanding and delineation of the general trends and to assess the likelihood of local dielectric breakdown. In addition, the extent of electromechanically induced deformation is studied using the distributions of the hydrostatic stress and von Mises equivalent stress in the microstructures.

II. MATERIALS AND MICROSTRUCTURES

To systematically analyze the effects of microstructural heterogeneities on the energetic composite’s sensitivity to dielectric breakdown, several mesoscale models with explicit resolution of the microstructure are computationally designed and generated as shown in Fig. 1. The microstructures have a HE crystal volume fraction \( \eta = V_{c} / V_{Ω} \), where \( V_{c} \) is the cumulative volume of the HE crystals and \( V_{Ω} \) is the total volume of the composite) between 30% and 60%. Furthermore, two crystal size distributions with a median size (\( d_{m} \)) of 240 and 80 \( \mu \)m are examined.

Both size distributions are approximately Gaussian in nature and are shown in Fig. 2. The microstructure generation uses Voronoi tessellation to establish a library of crystals as previously described.\textsuperscript{4,11,47} The technique uses the library of crystals to compose the microstructures. The crystals have random convex polyhedral shapes typical of HE crystallites in morphology. The size distribution and volume fraction of each microstructure are controlled by selecting crystals from the library that conform to prescribed statistical requirements. The binder in the microstructures is PVDF, a semi-crystalline fluoropolymer that displays piezoelectricity in its poled state. The \( d_{m} \) of the PVDF binder is aligned upward.

The material properties of the constituents are shown in Tables I and II. In Table I, \( ρ, \psi/E_{0}, K_{hd}, E, \nu, \) and \( σ_{f} \) represent the mass density, the dielectric constant, the dielectric breakdown strength, Young’s modulus, Poisson’s ratio, and the yield stress, respectively. In Table II, the five \( d_{i} \) constants denote the non-zero components of the piezoelectric tensor coefficients. Here, the “123” index notation corresponds to the local coordinate system of the material, where the 1, 2, and 3 axes denote the x (horizontal), y (vertical), and z (vertical) directions.
z (out of plane), and y (vertical, or the direction of the applied \( E \)-field) directions, respectively. Due to the lack of data on the full piezoelectric components for RDX, PETN, and HMX, \( d_{31} \) and \( d_{15} \) have been approximated by ensuring that they would have the same ratios of \( d_{31}/d_{33} \) and \( d_{15}/d_{33} \), respectively, of the PZT-5H. Furthermore, \( d_{32} \) and \( d_{24} \) have been assumed to be equal to the \( d_{31} \) and \( d_{15} \) components, respectively.

### III. MODEL CONFIGURATION AND BOUNDARY CONDITIONS

The electrostatic excitation is applied in the form of an external potential difference (2\( \varphi_0 \)) between the top and bottom surfaces of the microstructure, as shown in Fig. 3. Since the microstructure is a square with a side length of \( L = 4 \) mm, the nominal applied \( E \)-field is \( E_0 = 2\varphi_0/L \). The left and right surfaces are electrically charge-free. The model is two-dimensional and the plane-strain condition is assumed. For specificity, a sample thickness has been specified and is equal to \( L \). The boundary condition along the left and bottom surfaces of the microstructure is such that there is no normal displacement perpendicular to these surfaces while tangential displacement parallel to these surfaces are possible (the so-called “roller boundary condition”). The top and right surfaces of the microstructure are traction-free. All constituents are initially stress-free and at rest. Moreover, for the analysis of the response under mechanical excitation, a pair of compressive forces (\( F_0 \)) is applied on the top and bottom surfaces, resulting in an average stress of \( \sigma_0 = -F_0/L^2 \). The above analysis framework has been implemented entirely using COMSOL Multiphysics (v5.4).

### IV. GOVERNING EQUATIONS AND CONSTITUTIVE RELATIONS

The electrical response of the material is governed by the conservation of charge (Gauss’s law). The mechanical response is governed by the conservation of momentum. The equations are

\[
\begin{align*}
\text{div}(D) &= \nabla \cdot D = \varphi_0, \\
\text{div}(\sigma) &= \nabla \cdot \sigma = -b, 
\end{align*}
\]  

(1)

### TABLE I. Physical, dielectric, and elastic properties

<table>
<thead>
<tr>
<th>Material</th>
<th>( \rho ) (kg/m(^3))</th>
<th>( \varepsilon_{ij}/\varepsilon_0 )</th>
<th>( E_{bd} ) (MV/m)</th>
<th>( E ) (GPa)</th>
<th>( \nu )</th>
<th>( \sigma_y ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>1780</td>
<td>7.7</td>
<td>200</td>
<td>2.01</td>
<td>0.27</td>
<td>\ldots</td>
</tr>
<tr>
<td>RDX</td>
<td>1800</td>
<td>4.7</td>
<td>21.7</td>
<td>15.1</td>
<td>0.28</td>
<td>82</td>
</tr>
<tr>
<td>HMX</td>
<td>1910</td>
<td>3.08</td>
<td>14.6</td>
<td>15.3</td>
<td>0.32</td>
<td>125</td>
</tr>
<tr>
<td>PETN</td>
<td>1774</td>
<td>3.5</td>
<td>16.1</td>
<td>11.4</td>
<td>0.30</td>
<td>60</td>
</tr>
<tr>
<td>AP</td>
<td>1950</td>
<td>5.1</td>
<td>50</td>
<td>17.3</td>
<td>0.33</td>
<td>207.8</td>
</tr>
<tr>
<td>PZT-5H</td>
<td>7500</td>
<td>3220</td>
<td>12.7</td>
<td>61.1</td>
<td>0.39</td>
<td>60</td>
</tr>
</tbody>
</table>

Note: \( \varepsilon_0 \) denotes the absolute dielectric permittivity of free space (vacuum).

### TABLE II. Piezoelectric coefficients

<table>
<thead>
<tr>
<th>Material</th>
<th>( d_{31} ) (pC/N)</th>
<th>( d_{32} ) (pC/N)</th>
<th>( d_{33} ) (pC/N)</th>
<th>( d_{15} ) (pC/N)</th>
<th>( d_{24} ) (pC/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>21</td>
<td>1.5</td>
<td>-32.5</td>
<td>-27</td>
<td>-23</td>
</tr>
<tr>
<td>RDX</td>
<td>-0.02</td>
<td>-0.02</td>
<td>0.05</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>HMX</td>
<td>-0.13</td>
<td>-0.13</td>
<td>0.29</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td>PETN</td>
<td>-0.15</td>
<td>-0.15</td>
<td>0.32</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>PZT-5H</td>
<td>-274</td>
<td>-274</td>
<td>593</td>
<td>741</td>
<td>741</td>
</tr>
</tbody>
</table>

Fig. 2. Crystal size distributions (a) for the microstructures in Figs. 1(a)–1(d) with a median size of 240 \( \mu \)m and (b) for the microstructure in Fig. 1(e) with a median size of 80 \( \mu \)m.
where $D$ and $q_v$ denote the electric displacement vector and free-charge density per unit volume, respectively, and $\sigma$ and $b_v$ denote the mechanical stress tensor and body-force vector per unit volume, respectively. In the present analysis, $b_v = 0$.

The electric displacement consists of a piezoelectric polarization term caused by mechanical stress and a dielectric polarization term (induced dipole moment) caused by local electric field. The constitutive relation is

$$D_i = d_{ikl} \sigma_{kl} + \psi_{ik} E_k,$$  

where $E_k$ represents electric field vector and $d_{ikl}$ and $\psi_{ik}$ represent the piezoelectric coefficient and absolute permittivity tensors, respectively. An isotropic permittivity is assumed for all constituents of the microstructure. The electric field can be further expressed as $E_k = -\partial \varphi / \partial x_k$, where $\varphi$ denotes the scalar electric potential field in the material. The strain consists of a mechanical term and a piezoelectric term, such that

$$\varepsilon_{ij} = S_{ijkl} \sigma_{kl} + d_{ijkl} E_k,$$  

where $\varepsilon_{ij}$ and $\sigma_{kl}$ represent the Green–Lagrangian strain and the second Piola–Kirchhoff stress tensors, respectively, and $S_{ijkl}$ denotes the elastic compliance tensor. The strain tensor is related to the displacement via

$$\varepsilon = \frac{1}{2} (F^T F - I) = \frac{1}{2} [ (\nabla u)^T + (\nabla u)^T (\nabla u) ](\nabla u),$$  

where $F$ and $I$ represent the deformation gradient and the identity tensors, respectively, and $u = u(x)$ represents the displacement vector at material point $x$.

Rate-dependence of the constitutive behaviors is not considered since the quasi-static responses are assumed. The coupled electromechanical constitutive relation for Eq. (3) can be alternatively written as

$$\sigma_{ij} = S_{ijkl} (\varepsilon_{kl} - d_{mkl} E_m) = C_{ijkl} (\varepsilon_{kl} - d_{mkl} E_m),$$

where $C_{ijkl}$ represents the elastic stiffness tensor.

V. RESULTS AND DISCUSSION

A. Induced mechanical and electrical fields under electrostatic excitation

To understand the mechanical and electrical responses of the materials at the microstructure level, we first focus on the RDX/PVDF composite system with the microstructure profiles in Fig. 1, which have a range of HE grain fraction and different grain sizes. Subsequently, the responses of the same microstructures with the same PVDF binder but with the RDX grains replaced successively by HMX, PETN, and AP are discussed. Also discussed later is the response of an RDX/PVDF composite [60% RDX, Fig. 1(d)] with PZT-5H microparticles embedded in the binder.

The mechanical response is studied by analyzing the stress and strain fields induced by the applied electrostatic excitation via

FIG. 3. Schematic illustration of the mechanical and electrical boundary conditions for the microstructure model. The crystal/binder microstructure (4 × 4 mm² in size) shown above has a crystal volume fraction of $\eta = 60\%$. 
the piezoelectricity of the PVDF binder and the RDX crystals. As shown in Fig. 3, each microstructure is constrained at the left and bottom surfaces, and an external electrostatic field is applied along the upward direction. Figure 4 shows the distributions of hydrostatic stress ($\sigma_{\text{hyd}}$), von Mises equivalent stress ($\sigma_{\text{eq}}$), and volumetric strain ($\varepsilon_{\text{vol}}$) in an RDX/PVDF sample under an applied nominal $E$-field of $E_0 = 21.7$ MV/m for the microstructure in Fig. 1(d). This $E$-field is equal to the breakdown strength ($E_{\text{bd}}$) of the RDX crystal.\textsuperscript{48–51} Under this applied field, the equivalent stress in the RDX crystals is determined to be far below the yield stress of $\sigma_y = 82$ MPa for RDX. Hence, the induced electromechanical stresses and strains (i.e., the converse piezoelectric effect) due to an external electric field alone are low and are unlikely to result in significant heating or failure that may lead to ignition. Therefore, the present analysis focuses on the electric field in the materials and the likelihood of dielectric breakdown as the potential mechanism for ignition control under the applied $E$-field.

Figure 5 shows the electrostatic fields for the same RDX/PVDF microstructure under the same condition as shown in Fig. 4. Compared with the PVDF binder, the RDX crystals experience
higher $E$-field magnitude ($|E|$), lower electric displacement magnitude ($|D|$), and lower electrostatic energy density [$\varepsilon_{el} = (E \cdot D)/2$], owing to the lower permittivity of the crystals.

**B. Determination of the likelihood of dielectric breakdown within the HE crystals**

The analysis of the likelihood of dielectric breakdown in the energetic crystals is carried out by evaluating the fraction of the volume of the crystals (not including the binder as the binder is very unlikely to experience breakdown under the conditions analyzed) whose local electric field reaches or exceeds the breakdown strength. The analysis here focuses on the electrostatic potential and $E$-field without direct simulation of the dielectric breakdown process; therefore, the analysis applies to the response leading up to the breakdown in the crystals. Although the breakdown process within the sample is not explicitly modeled, the analysis here enables the quantification of the likelihood of breakdown by evaluating how much of the microstructure reaches or exceeds the constituents’ breakdown strength as the applied $E$-field is increased. Note that the breakdown strength of the HE crystals is significantly lower than that of the PVDF binder, and hence, breakdown is practically always expected in the crystals. Hence, the analysis focuses on the crystals.

The probability of dielectric breakdown within the sample is defined as the volumetric ratio of the HE crystals whose local $E$-field is equal to or greater than their corresponding breakdown strength, i.e.,

$$P = \frac{V_{gr}(|E| \geq E_{bd})}{V_{gr}} = \frac{V_{gr}(|E| \geq E_{bd})}{\eta V_{\Omega}},$$  \hspace{1cm} (6)

where $V_{gr}$ is the volume of the grains, $V_{gr}(|E| \geq E_{bd})$ is the part of $V_{gr}$ that experiences $E$-fields at or above the crystals’ breakdown strength ($E_{bd}$), and $V_{\Omega}$ is the total volume of the microstructure.

**C. Effect of crystal volume fraction on the likelihood of dielectric breakdown**

This probability is expressed in terms of both the cumulative density function ($P$) and the probability density function ($p$) in Fig. 6. The horizontal axis represents the applied $E$-field ($E_0 = \Delta\varepsilon/L$) divided by the breakdown strength of the energetic crystals (RDX in this case). The microstructures considered are shown in Figs. 1(a)–1(d). Obviously, the peak local $E$-field is always higher than the applied $E$-field, owing to the non-uniform nature of the fields. Under the same applied $E$-field, the probability of breakdown is higher for lower crystal fraction as the permittivity of the crystals is lower than that of the PVDF binder.

In Fig. 7, the peak enhancement of electric field in the RDX crystals is also calculated for the cases in Fig. 6, which have crystal fractions between 30% and 60%. This peak enhancement is computed by dividing the threshold $E$-field value that exceeds the $E$-field strength in 95% of the HE crystals by the applied $E$-field. Here, the 95% threshold is used to avoid spurious results associated with the use of the highest $E$-field value. This figure quantifies the dependence of the overall level of $E$-field in the crystals on the crystal fraction of the microstructures. The peak $E$-field enhancement in the crystals is greater than one for all volume fractions examined, with the peak enhancement ranging between 1.30 and 1.18 for $\eta = 30$%–60% (RDX/PVDF), respectively.

Together, Figs. 6–8 demonstrate the effect of crystal volume fraction (between 30% and 60%) on the breakdown sensitivity of RDX/PVDF composites. Here, it is evident that HE crystals in a microstructure with a low crystal fraction are likely to experience
higher levels of peak $E$-field, thus augmenting the likelihood of dielectric breakdown. The reason for this trend is that the energetic crystals (RDX in this case) have a considerably lower permittivity than the binder. This mismatch in dielectric constants causes the crystals to experience local $E$-fields higher than those experienced by the binder, at levels that are even higher than the applied field of $E_0$.

### D. Effect of crystal size on the likelihood of dielectric breakdown

The effect of crystal size is analyzed using the RDX/PVDF microstructures in Figs. 1(d) and 1(e). The corresponding size distributions are shown in Fig. 2. Both microstructures have the same crystal fraction of $\eta = 60\%$. The areas of the HE crystals with local $E$-field equal to or above the breakdown strength under an applied $E$-field of $E_0 = 0.9E_{bd}$ are shown in Figs. 9(a) and 9(b) for the two microstructures [median: 240 $\mu$m [large, Fig. 9(a)] and 80 $\mu$m [small, Fig. 9(b)]]. The corresponding breakdown probability density distributions in Fig. 9(c) are very similar to each other, indicating that the sensitivity to dielectric breakdown is not significantly influenced by crystal size in the range analyzed, but rather it is the crystal fraction that dominates the behavior.
E. Effect of dielectric permittivity of HE crystals on the likelihood of breakdown

In addition to the RDX/PVDF constituent combination, composites with 60% HMX, PETN, and AP crystals and 40% PVDF binder are also analyzed to delineate the effects of different HE crystals. To carry out the comparative analyses, the microstructure shown in Fig. 1(d) is considered. The results are compared in Figs. 10 and 11. The HMX/PVDF composite is the most prone to dielectric breakdown. The reason for this is that HMX has the lowest permittivity among the crystals considered here (see Table 1), making it the most strongly polarized (experiencing the highest $E$-field) under the same external field. The effect of dielectric permittivity on the $E$-field enhancement of the HE crystals can also be seen in Fig. 11. The peak $E$-field enhancement (i.e., based on the top 5% value similar to that in Fig. 7) of the crystals decreases as the permittivity increases. The composite with HMX crystals ($\psi = 3.08\varepsilon_0$) experiences a peak field enhancement that is $\sim$17% higher (1.34 vs 1.15) than that of the composite with AP crystals ($\psi = 5.1\varepsilon_0$).
F. Effect of binder-embedded with PZT particles on the likelihood of dielectric breakdown

To explore avenues for enhancing the piezoelectric effect in the composites, microparticles of piezoelectric PZT-5H are embedded in the PVDF binder. This analysis is motivated by the experiments of Reese et al.\textsuperscript{41} in which nanoparticle inclusions have been encapsulated inside energetic crystals. For this study, the same RDX/PVDF microstructure in Fig. 1(d) is used. As shown in Fig. 12, the microparticles are 8 μm squares and have a volume fraction between 0% and 6%. Randomly distributed throughout the PVDF binder, these particles are initially poled along the vertical direction, which is also the direction of the applied $E$-field.

Figure 13 shows the distributions of electric field magnitude ($|E|$) and electric displacement magnitude ($|D|$) for an RDX/PZT/PVDF composite (60%, 6%, and 34%, respectively, by volume). Under an applied field of $E_0 = E_{bd}$ (21.7 MV/m), the PZT microparticles experience a relatively low electric field due to their markedly high permittivity (see Table I), or resistance to external $E$-field.

Figure 14 shows the differences in the $E$-field in the RDX crystals under an applied $E$-field of $E_0 = 0.85E_{bd}$ for PZT fractions ranging between 0% and 6%. As expected, the local $E$-field in the RDX crystals increases as the PZT level is increased. This is due to the fact that the introduction of a strong dielectric (PZT-5H in this case) into the composite leads to significant polarization, thereby amplifying the local electric field within the crystals.

The probability and probability density of breakdown are shown as a function of the applied $E$-field in Figs. 15(a) and 15(b), respectively, for RDX volumes between 0% and 6%. The rate of increase of the cumulative probability or the peak probability density is highest at the median applied field in Fig. 15(b), because the distributions closely track normal distributions. As shown in Fig. 16, the median applied $E$-field for breakdown, and therefore likelihood of RDX crystal breakdown due to the applied $E$-field, decreases as the PZT fraction increases. The standard deviations of the probability
FIG. 13. Electric field magnitude (left) and electric displacement magnitude (right) in the RDX(60%)/PZT(6%)/PVDF(34%) microstructure shown in Fig. 12 under an applied $E$-field of $E_0 = E_{bd}$ (21.7 MV/m). Only a portion of the microstructure is shown for clarity.

FIG. 14. Upper row: Distributions of $E$-field magnitude normalized by the breakdown strength of RDX for RDX/PZT/PVDF microstructures with different PZT fractions as shown in Fig. 12. Lower row: Areas of the RDX crystals (marked in red) with local $E$-field at or above the breakdown strength $E_{bd}$ of RDX (21.7 MV/m). The applied $E$-field is $E_0 = 0.85E_{bd}$ in the vertical direction. The volume fractions of binder-embedded PZT microparticles considered are 0%, 2%, 4%, and 6%. The RDX volume fraction is $\eta = 60\%$ in all cases.
distributions are also summarized in Fig. 16. The median decreases from 0.92 to 0.875 while the standard deviation increases from 0.044 to 0.081, as the PZT level increases from 0% to 6%.

G. Strain energy and electrostatic energy

The applied $E$-field imparts energy into the material in the forms of electrostatic energy and strain energy. The partitioning of the electromechanical energies is analyzed. The analysis uses the average electrostatic energy density $\bar{\varepsilon}_d$ (electrical) and the average strain energy density $\bar{\varepsilon}_m$ (mechanical) in the microstructures, which are defined, respectively, as

$$\bar{\varepsilon}_d = \frac{1}{V_0} \int_{V_0} \varepsilon_d \, dV = \frac{1}{V_0} \int_{V_0} \varepsilon_{el} \cdot dD, \quad \text{and} \quad \bar{\varepsilon}_m = \frac{1}{V_0} \int_{V_0} \varepsilon_m \, dV = \frac{1}{V_0} \int_{V_0} \varepsilon_{me} \cdot d\sigma.$$  

(7)

Figure 17 shows the correlation between $\bar{\varepsilon}_d$ and $\bar{\varepsilon}_m$ for the microstructures in Figs. 1(a)–1(d) as the applied $E$-field is varied from 0 to 10 MV/m. In Fig. 17(a), the RDX/PVDF composite with 30%–60% RDX is examined. In each case, the two forms of energy increase proportionally. As the fraction of RDX increases, the strain energy density $\bar{\varepsilon}_m$ decreases and the electrostatic energy $\bar{\varepsilon}_d$ increases [Fig. 17(a)], since the piezoelectric coefficients ($d_{ij}$) of the RDX are smaller than those of the strongly piezoelectric PVDF. Figure 17(b) shows the partitioning of the energies at different concentrations of PZT particles (microstructures in Fig. 14). The fraction of the strain energy increases slightly as the PZT content increases from 0% to 6% PZT ($\bar{\varepsilon}_{me} = 15.4 \text{ J/m}^3$ for 0% PZT and $\bar{\varepsilon}_{me} = 18.4 \text{ J/m}^3$ for 6% PZT under an applied $E$-field of 10 MV/m). This indicates that the addition of strongly piezoelectric particles (Table II) can enhance the overall electromechanical deformation of the microstructure, but only slightly. When different HE crystals are used, Fig. 17(c) shows that the AP/PVDF composite ($\eta = 60\%$) has the highest electrostatic energy density as the AP crystal has the highest relatively high permittivity among the crystals considered.

H. Response to mechanical excitation: Stress and electric fields

The preceding analyses have concerned the responses of the materials to electrostatic excitation. There is also an interest in
understanding how the materials respond to an external mechanical loading. To explore this effect, the RDX/PVDF composite in Fig. 1(d) is used. The mechanical excitation is effected by applying a quasi-static (i.e., slow), compressive stress of $\sigma_0 = -25 \text{ MPa}$ at the top and bottom surfaces. To put it in perspective, this stress level is below the yield stress of the RDX ($\sigma_y = 82 \text{ MPa}$) (see Table I). It is useful to note that this particular stress level may appear to be arbitrary.

However, since all constituent responses are linear and rate-independent, results can be scaled for other levels of applied excitation. Furthermore, all constituents are assumed to be well-bonded so as to preclude any interfacial slip across the material boundaries, and hence, the triboelectric effects have not been considered in this study.

Figure 18 shows the fields of the von Mises equivalent stress ($\sigma_{eq}$) and the magnitude of the induced $E$-field ($|E|$) in the crystals.
in response to the applied stress. Although the applied stress is well below the yield stress of the RDX crystals, it is sufficient to cause yielding in some areas of RDX [Fig. 18], signifying that mechanical stress (especially rapidly applied loading) can be used as a means to induce significant deformation and heating, which can lead to potential chemical reaction initiation. On the other hand, the induced E-field is far below the dielectric breakdown strength of the crystals, suggesting that dielectric breakdown would not be a likely mechanism for obtaining hotspots and subsequent ignition under mechanical loading.

To put this in further perspective, Fig. 19 shows the probability of yielding and probability of breakdown as functions of \( \sigma_0/\sigma_\eta \) (applied stress \( \sigma_0 \) normalized by the yield stress of the HE crystals \( \sigma_\eta \)). While the probability of yielding is high even for \( \sigma_0/\sigma_\eta < 1 \), the probability of breakdown reaches a non-trial level of \( \approx 10\% \) only when \( \sigma_0/\sigma_\eta > 3.5 \). At this applied stress level, however, the HE crystals will have fully yielded. In summary, under mechanical loading mechanical deformation and failure are the likely mechanisms for manipulating the behavior of the EM rather than dielectric breakdown.

VI. SUMMARY AND CONCLUSION

This paper provides a first-ever analysis of the effect of piezoelectricity on the behavior of several energetic composites that consist of HE crystals embedded in a matrix of PVDF binder. The piezoelectricity comes from the HE crystals themselves, the PVDF, and in some cases PZT microparticles embedded in the PVDF binder. The HE crystals considered include RDX, HMX, PETN, and AP. The analyses focus primarily on the responses of the composites due to an applied electrostatic excitation, while a simple analysis has also been performed to study the response under an applied mechanical excitation. The primary interest is mechanisms that may lead to hotspot formation that can cause initiation of chemical response in the HE crystals. Overall, under electrostatic excitation, the likely mechanism for hotspot formation is dielectric breakdown in the HE crystals since the induced stress levels are very low for applied \( E \)-fields up to the dielectric breakdown strength of the crystals. On the other hand, under mechanical stress, the likely mechanism for hotspot formation is yielding, deformation, and failure since the induced \( E \)-field is far below the breakdown strength of the HE crystals. The microstructure heterogeneities and constituent properties significantly affect the responses obtained. In general, both the local \( E \)-field and the stress in the microstructures are magnified relative to the applied field or stress. This is the underlying factor for the obtained responses. Among the crystals analyzed, HMX exhibits the strongest enhancement of local electric field when subjected to a moderate level of applied \( E \)-field (i.e., \( E_0/E_{bd,i} < 1 \)). The ranking order for all crystals analyzed is HMX, PETN, RDX, and AP, as crystals with low permittivity result in a high probability of breakdown.

Under electrostatic excitation, higher volume fractions of a HE crystal correspond to lower probability of dielectric breakdown. Changing the HE crystal size in the range of 80–240 \( \mu \)m does not significantly affect the response. The addition of PZT microparticles enhances the dielectric responses and, therefore, the likelihood of breakdown, due to their high dielectric permittivity which enhances the \( E \)-field in adjacent HE crystals, not because of their piezoelectricity. As such, they may be used as a means to manipulate the properties of energetic materials.

It is useful to point out that, as a first study on the subject, the analyses carried out do not consider the breakdown or yielding. Rather, the analyses focus on the levels of \( E \)-field and stress and their respective relations to the breakdown strength and yield stress of the HE crystals. As such, the trends in responses and the likelihood are explored. Future analyses can use the findings to focus on factors that are most efficient in leading to possible hotspots. For example, under electrostatic excitation, altering the type of HE crystals and crystal volume fractions should be prioritized over altering the size scale of the crystals. Also, RDX is a better candidate than the other crystals discussed. Finally, future analyses can also explicitly track breakdown and yielding.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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