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Nanocomposites with enhanced dielectric permittivity and breakdown strength by microstructure design of nanofillers

Ziming Cai [a], Xiaohui Wang [a, *], Bingcheng Luo [a], Wei Hong [b, c], Longwen Wu [a], Longtu Li [a, **]

[a] State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China
[b] Department of Aerospace Engineering, Iowa State University, Ames, IA 50010, USA
[c] Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan

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ABSTRACT

Polymer-ceramic nanocomposites play an essential role in pulsed power system, due to their ultrahigh power density and fast charging–discharging capability. They also hold strong potential for improving the performance in energy storage capacitors, hybrid electric vehicles and kinetic energy weapons, since they contain a high-breakdown-strength polymer matrix and high-dielectric-permittivity ceramic nanofillers and thus can reach a high level of energy-storage density. In this work, through a finite element method and a phase field model, we theoretically analyze the nanocomposites with enhanced dielectric permittivity and dielectric breakdown strength by microstructure design of ceramic nanofillers, which covers the orientation, morphology and arrangement of nanofillers. Results indicate that the orientation of ceramic nanofibers has significant influence on the dielectric permittivity and breakdown strength of nanocomposites. The comparison of nanoparticles and nanofibers reveals the increase extent of interactions between polymer matrix and ceramic nanofillers can enhance the dielectric breakdown strength of the nanocomposites. Based on the results above, two sandwich structures consisting of both nanoparticles and nanofibers have been constructed to pursue a higher energy storage density.

1. Introduction

Dielectric materials possess fast charging-discharging capability and high power density, which are critical for the application in pulsed power system [1,2]. However, the low energy density limits their application in energy storage capacitors, hybrid electric vehicles and kinetic energy weapons [3–5]. In principle, the energy-storage density (J) of these devices can be written as

$$J = \int_0^{D_{max}} EdD \tag{1}$$

where E is electric field strength, D is dielectric displacement, and D_{max} is the dielectric displacement under saturated electric field strength. If we take dielectric permittivity ε as constant, the formula can be convert to

$$J = \frac{1}{2}\varepsilon {E_B}^2 \tag{2}$$

We can summarize that the dielectric permittivity (ε) and breakdown electric field (E_B) are two major factors that determine the energy storage density of dielectric materials. Polymer-ceramic nanocomposites show superior advantages to all other candidates, since that polymers are known for their high breakdown strength, meanwhile ceramic hold high dielectric permittivity [6–11]. Recent developments in polymer composites with nanosized ceramic fillers have reached high permittivity, high dielectric breakdown strength, low dielectric loss and long cycle life [12–21]. A maximum energy density of $> 30\ J/cm^3$ has been achieved in P(VDF-HFP)/BTO@TO_nfs nanocomposites [22]. The volume fraction, morphology, size, aspect ratio and orientation of ceramic nanofillers have been reported to have significant effect on the dielectric

* Corresponding author.
** Corresponding author.
E-mail addresses: wxh@mail.tsinghua.edu.cn (X. Wang), llt-dms@mail.tsinghua.edu.cn (L. Li).

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permittivity and breakdown strength of nanocomposites [23–28], thus a property microstructure design of ceramic naonofillers is necessary for nanocomposites to obtain higher energy density.

In this work, we theoretically analyze the nanocomposite with enhanced dielectric permittivity and dielectric breakdown strength by microstructure design of ceramic nanofillers based on a finite element method and a phase field model, both implemented in COMSOL Multiphysics 5.2a. The structural design of the composite covers the orientation, morphology and arrangement of nanofillers [27–30]. The morphology of nanofillers used in our numerical model are nanofibers and nanoparticles, which are the most common nanofillers in previously reported works [31–34]. Firstly, four nanocomposites with different oriented nanofibers are simulated and compared. The effect of nanoparticles distribution in polymer matrix on the dielectric permittivity and breakdown strength on nanocomposites was studied in our previous work [35]. After that, the dielectric permittivity and breakdown strength of nanocomposites with preferred oriented nanofibers and with well distributed nanoparticles are separately calculated. It is found that under the same content of nanofillers, nanocomposite filled with well distributed nanoparticles (NNP) displays a higher dielectric permittivity, while nanocomposite filled with preferred oriented nanofibers (NNF) indicates a higher breakdown strength. Based on this conclusion and other related work [36–39], two sandwich-structured nanocomposite including both polymer/nanofibers layer and polymer/nanoparticles layer have been constructed to obtain both high dielectric permittivity and high breakdown strength, thus achieve high energy storage density.

2. Modeling process

2.1. Landau theory on ferroelectric ceramic nanofillers and phase field method on dielectric breakdown

The side length (L) of selected square region (R) of nanocomposites is set to 10 μm. As examples, two widely used filler and matrix materials, a ferroelectric ceramic barium titanate (BT) and a dielectric polymer poly(vinylidene fluoride) (PVDF) are adopted in our following calculations. The nanocomposites can be taken as a ferroelectric-dielectric system, for which the polymer matrix can be seen as linear dielectric, while the ceramic nanofillers are considered non-linear ferroelectric. The dielectric behavior of BT can be described through Landau's theory of phase transformation [40], which reads

$$\Delta G = \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 - EP, \tag{3}$$

where P is the polarization, E is the applied electric field, and α, β and γ are the dielectric stiffness coefficients [40]. In stress-free polymer matrix, the equation of state of the electric field dependence of polarization and the dielectric response and its stability parallel to the applied electric field are given by Ref. [41].

$$\frac{\partial \Delta G}{\partial P} = 0 = \alpha P + \beta P^3 + \gamma P^5 - E, \tag{4}$$

$$\varepsilon_r(E) = \frac{1}{\varepsilon_0(\alpha + 3\beta P^2 + 5\gamma P^4)}, \tag{5}$$

$$\eta(E) = \frac{\varepsilon_r(E) - \varepsilon_r(E=0)}{\varepsilon_r(E=0)}. \tag{6}$$

The dielectric response of nanocomposites is simulated using COMSOL Multiphysics. The effective dielectric permittivity can be calculated from Ref. [42].

$$\varepsilon_r = \mathrm{d}\frac{\int D\cdot E\mathrm{d}V}{\varepsilon_0 A U^2}. \tag{7}$$

The study of the dielectric breakdown process of nanocomposites follows closely the phase field model developed in Refs. [43,44], by drawing an analogy between dielectric breakdown and mechanical fracture. A huge advantage of this method is that it can visualize the breakdown pathways and calculate the normalized breakdown strength. Instead of tracking individual breakdown pathways, a continuous scalar phase field s (x, t) is introduced to characterize the evolution process of a dielectric medium which turns into conductive at full damage. The value of s varies from 1 to 0, which respectively represent the intact state and the fully damaged state. The fully damaged material becomes conductive. Numerically, a large but finite permittivity ε_0/η is taken for such material part, where ε_0 is the initial permittivity and η is a small enough number. For any other intermediate state of nanocomposites, the permittivity is interpolated by

$$\varepsilon(s) = \frac{\varepsilon_0}{f(s) + \eta}, \tag{8}$$

where $f(s) = 4s^3 - 3s^4$. Breakdown happens if the process decreases the total potential energy of the system

$$\Pi[s,\phi] = \int_{\Omega} [W_{es}(E,s) + W_d(s) + W_i(\nabla s)]\mathrm{d}V, \tag{9}$$

where $W_{es}(E,s) = -\frac{\varepsilon}{2}E\cdot E$ is the complementary electrostatic energy per unit volume, $W_d(s) = W_c[1 - f(s)]$ is the breakdown energy function with W_c representing the critical density of electrostatic energy, $W_i(\nabla s) = \frac{\Gamma}{4}\nabla s\cdot\nabla s$ is the gradient energy term to regulate sharp phase boundaries. It is worth noting that the material parameter Γ is approximately the breakdown energy [41]. According to linear kinetic law: $\partial s/\partial t = -m\delta\Pi/\delta s$, the evolution equation for breakdown variable s can be achieved after substituting in detailed forms of the energy functions:

$$\frac{1}{m}\frac{\partial s}{\partial t} = \frac{\varepsilon'(s)}{2}\nabla\phi\cdot\nabla\phi + W_c f'(s) + \frac{\Gamma}{2}\nabla^2 s. \tag{10}$$

Here, mobility m is a material parameter that features the speed of breakdown propagation in nanocomposites. To facilitate numerical simulation, we will normalize energies by Γ, time by mΓ, and electric potentials by $\sqrt{\Gamma/\varepsilon_0}$. The normalized governing equations of dimensionless form can be written as:

$$\overline{\nabla}\cdot\left[\frac{1}{f(s) + \eta}\overline{\nabla\phi}\right] = 0, \tag{11}$$

$$\frac{\partial s}{\partial \bar{t}} = -\frac{f'(s)}{2[f(s)+\eta]^2}\overline{\nabla\phi}\cdot\overline{\nabla\phi} + f'(s) + \frac{1}{2}\overline{\nabla}^2 s, \tag{12}$$

in which the corresponding quantities are symbolized with overbars. While the above described model considers only linear dielectrics, here in this study we add the nonlinear performance of nanoceramic by normalizing Eqs. (4) and (5) into:

$$\alpha\overline{P} + \beta\overline{P}^3 + \gamma\overline{P}^5 - \overline{E} = 0, \tag{13}$$