

# Modeling effect of nanofillers on charge transport in composite polymer films for energy storage



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## ABSTRACT

The effects of dielectric and conducting nanofiller size, loading, and electric field on bipolar charge injection, transport, and recombination (or electroluminescence) through amorphous polymer are studied. Versions of 3D particle-in-cell model based on the classical electrical double layer representation are used to treat the conducting and dielectric nanoparticles. Metal–polymer charge injection assumes Schottky emission and Fowler–Nordheim tunneling, migration through field-dependent Poole–Frenkel mobility, and recombination with Monte Carlo selection based on collision probability. A boundary integral equation method is used for solution of the Poisson equation coupled with a second-order predictor–corrector scheme for robust time integration of the equations of motion. The stability criterion of the explicit algorithm conforms to the Courant–Friedrichs–Levy limit. Trajectories for charge that traverse the film are curvilinear paths that meander through the interspaces of the interaction zone. Compared to dielectric nanofillers, composite films with conducting nanofillers have: larger peaks and higher steady-state amplitudes for both injected currents and electrode  $E$  fields;  $<1/6$  of the attached charge fraction;  $>2x$  of the conduction charge fraction;  $>2x$  of the recombined charge fraction; all charge fractions change very rapidly at sizes below 10 nm; much higher loading of 21 vol.% versus 2 vol.%; and higher leakage conductivities of  $0.5 \times 10^{-14}$  S/cm and  $0.75 \times 10^{-14}$  S/cm with bipolar and unipolar charge, respectively, where the value for the dielectric nanofiller is  $\sim 0.2 \times 10^{-14}$  S/cm. Effective permittivities computed using a new energy conservation method is shown to have excellent agreement compared with established Lichtenecker, Bruggeman, and Maxwell–Garnett mixing rules. Computed stored energies show monotonic increase with dielectric fillers and a peak at 25 vol.% for conducting fillers which may be attributed to the competing effects of higher energy with increasing field modification and lower energy with decreasing binder volume.

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## 1. Introduction

Nanocomposite films used in energy storage for rapid power cycling applications are fabricated by incorporating ceramic nanofillers within amorphous polymer binders. High permittivity ceramic nanofillers (with typically low breakdown strength) are combined with high breakdown strength polymers (with typically low permittivity) in the right proportion, size range, and polarization to result in nanocomposite films with high energy density,  $U_e$ , given by  $U_e = \int E dD$ , where  $E$  is the applied electric field and  $D$  is the electric displacement. Other beneficial properties include: low materials and replacement cost, self-healing,

lightweight, and small footprint. The notion is to combine the processability and high breakdown field strength of the polymer with the high dielectric constant of the fillers and engineer the film for low dielectric loss. However, large contrast in permittivity between the two phases give rise to highly inhomogeneous electric fields ( $E$ ) in the “interaction zone”, defined as the interfacial region that surrounds the nanofillers and interspaces. These  $E$  fields together with structural inhomogeneity generally lead to a significant reduction in the effective breakdown field strength of the composite, limiting the increase in the energy storage capacity and energy density. A key solution is to improve the dispersion of the filler in the polymer matrix to create effective electron scattering and transport centers, thus reducing breakdown probability by blocking degradation tree growth and increasing long-term breakdown strength [1]. The dielectric constant,  $k$ , of

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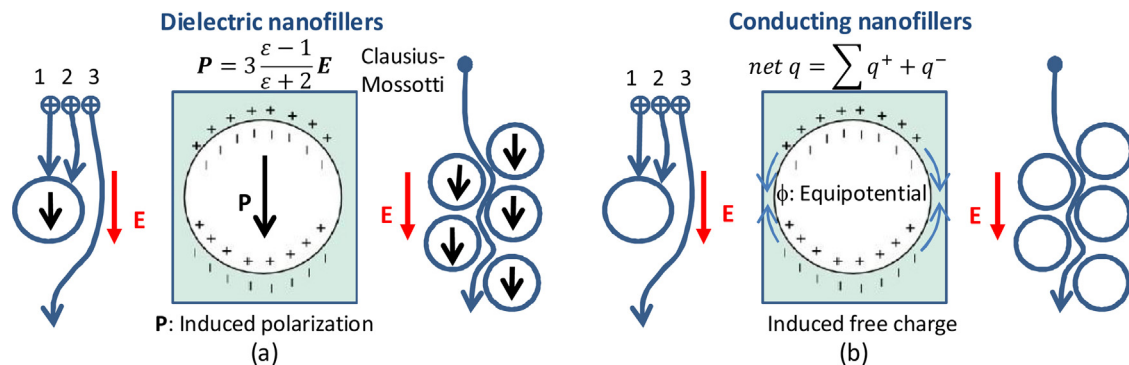
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composites can also be greatly improved by adding conductive or semiconductive nanofillers in the insulative polymer matrix. As the volume fraction,  $f$ , of the fillers increases to the vicinity of the percolation threshold,  $f_c$ ,  $k$  of the nanocomposite films can be described by the well-known power law,  $k/k_p \propto [f_c - f]^{-s}$ , where  $k_p$  is the dielectric constant of the polymer matrix and  $s$  is an exponent between 1 and 2. By staying below the percolation threshold, the dielectric constant of nanocomposites can be increased to tens or even hundreds of times the polymer matrix with conducting nanofillers.

Considerable progress has been made over the past several years in the enhancement of the energy densities of the polymer nanocomposites by tuning the chemical structures of ceramic fillers and polymer matrices and engineering the polymer–ceramic interfaces. For example, the incorporation of the TiO<sub>2</sub> nanoparticles into the polymer induces an improved electric displacement, which accounts for high energy densities observed in the nanocomposites [2]. The challenge in matching nanofillers with the polymer matrix is to understand the role of the interaction zone where the very large area to volume ratio of the interfaces in nanocomposites has significant impact on the electrical and dielectric properties of the film. Charge mapping studies may help to define and quantify the taxonomy of the mobile, trapped, bound, and polarization charge types and their abundance. Knowledge of the spatial and temporal distributions may facilitate insight into the dynamics of charge re-distributions which lead to breakdown at high fields or prolonged usage. Empirical methods using pulse electroacoustic (PEA) and laser induced pressure pulse (LIPP) techniques have demonstrated preliminary feasibility [3,4]. 1D bipolar charge transport models have described LDPE results [5,6]. Recently, a hybrid algorithm capable of handling leakage current up to pre-breakdown levels have been successfully applied to layered polymer films and successfully simulated PEA measurements [7]. Axisymmetric models capable of handling divergent field configurations have also been reported [8,9]. However, continuum charge transport models are not suited to simulate material with morphology at the nanometer length scale. Commercial software has been used to compute effective permittivity of nanocomposites [10,11]. Several models of nanoparticles are discussed in the literature, including the Tanaka Multicore 3-layer and the Lewis models [12]. The classical electrical double layer (EDL) is similar to the Lewis model and is predicated on a monopole net charge for the core. Charge transport is enabled by the increase in nanoparticle loading within the dielectric composite eventually leading to overlap of the diffuse double layers forming conduction paths. Bulk charge accumulation

is reduced due to this internal conductivity, and the dielectric breakdown strength of the nanocomposite is improved.

This paper simulates the use of dielectric Alumina (Al<sub>2</sub>O<sub>3</sub>) and conducting nanofillers in a polyamide/polyimide (PA/PAI) binder. The modeling is comprehensive, self-consistent, and novel because no similar work could be found in the literature. The EDL model is extended by substitution of a dipolar core and used for dielectric nanofillers as shown in Fig. 1(a) where the induced polarization aligns with the bias electric field. The classical EDL model is used for conducting nanofillers as shown in Fig. 1(b). Charge passage with dielectric nanofillers may be illustrated in Fig. 1(a), where incoming positive charge is repelled by the positive-end and attracted toward the negative-end of the dipole and vice-versa. Charge is allowed to attach on impact forming the bound Stern–Helmholtz layer. Subsequent waves of incoming charge are repelled to form the diffuse outer Gouy–Chapman transport layer. The cumulative charge buildup on opposing ends of the dipole leads to Maxwell–Wagner–Sillars (MWS) polarization. The gradual charge deposition and formation of the diffuse layers as charge migrates through the polymer film creates the interaction zone. Trajectories for charges that make it through the film to the counter-electrode are curvilinear paths that meander through the interspaces. The corresponding description for conducting nanofillers is shown in Fig. 1(b). For bipolar charge, the initial charge ‘1’ impacts the upper hemisphere of nanofiller followed by ‘2’ subject to recombination and net charge repulsion. In the unipolar case, Coulomb repulsion from net charge may repel subsequent particle ‘3’. Induced free charge and impacted charge create an equipotential surface on the nanofiller. Charges that arrive at the counter-electrode are neutralized and therefore contribute to the conduction of the film; but not to the field. Metal–polymer charge injection assumes Schottky emission and Fowler–Nordheim tunneling, migration through field-dependent Poole–Frenkel mobility, and recombination with Monte Carlo selection. A boundary integral equation method (BIEM) is used for solution of the Poisson equation coupled with a second-order predictor–corrector scheme for robust time integration of the equations of motion. The stability criterion of the explicit algorithm conforms to the Courant–Friedrichs–Levy (CFL) limit. This paper will predict bipolar charge injection, transport, and recombination/electroluminescence through nanocomposite film comprising dielectric Alumina and conducting nanofillers in amorphous polyamide/polyimide matrix for a range of nanofiller size, vol.% loading, and  $E$  field biases. A novel energy conservation method is used to compute effective permittivity and stored energy in composites with dielectric or conducting fillers for comparison.



**Fig. 1.** (a) Extended EDL model for dielectric nanofiller (e.g., Al<sub>2</sub>O<sub>3</sub>) in amorphous polymer (e.g., PA/PAI) matrix where initial charge ‘1’ attach to upper hemisphere of nanofiller followed by ‘2’ until Coulomb repulsion from charge build-up allow subsequent particle ‘3’ to pass resulting in MWS polarization effect; and (b) EDL model for conducting nanofillers in amorphous polymer where impacted bipolar charge migrate freely on the surfaces and recombine, resulting in equipotentials and Coulomb repulsion from net charge leading to particle trajectories meandering through the interspaces.

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