Polymer Nanocomposites for Electrical Energy Storage

Qing Wang,1 Lei Zhu2

1Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Philadelphia 16802
2Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106

Correspondence to: Q. Wang (E-mail: wang@matse.psu.edu) or L. Zhu (E-mail: lei.zhu2@case.edu)

Received 3 July 2011; revised 26 July 2011; accepted 27 July 2011; published online 17 August 2011
DOI: 10.1002/polb.22337

ABSTRACT: This review highlights the frontier scientific research in the development of polymer nanocomposites for electrical energy storage applications. Considerable progress has been made over the past several years in the enhancement of the energy densities of the polymer nanocomposites via tuning the chemical structures of ceramic fillers and polymer matrix and engineering the polymer–ceramic interfaces. This article summarizes a range of current approaches to dielectric polymer nanocomposites, including the ferroelectric polymer matrix, increase of the dielectric permittivity using high-permittivity ceramic fillers and conductive dopants, preparation of uniform composite films based on surface-functionalized fillers, and utilization of the interfacial coupling effect. Primary attentions have been paid to the dielectric properties at different electric fields and their correlation with film morphology, chemical structure, and filler concentration. This article concludes with a discussion of scientific issues that remain to be addressed as well as recommendations for future research. © 2011 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 49: 1421–1429, 2011

KEYWORDS: capacitors; dielectric properties; energy density; ferroelectric polymers; ferroelectricity; interfaces; nanocomposites; nanoparticles; organic–inorganic interfaces; polymer nanocomposites; poly(vinylidene fluoride); structure–property relations

INTRODUCTION

Advances in portable electronic devices, stationary power systems, and hybrid electric vehicles create demand for low-cost, compact, and high-performance electrical energy storage devices.1,2 Among various energy storage technologies including batteries, fuel cells, capacitors, and supercapacitors, capacitors possess the advantage of high power density due to the fast electrical energy storage and discharge capability. However, the energy density of capacitors, which is governed by the dielectric materials that separate the opposite static charges, is relatively low and falls significantly short of rising demand in advanced applications.

The introduction of inorganic nanoparticles into polymer matrices to form dielectric polymer nanocomposites represents one of the most promising and exciting avenues for the development of dielectric materials with high energy density. In general, the energy density of a dielectric material can be derived from

\[ U_e = \int E dD, \]

where \( E \) is applied electric field and \( D \) is electric displacement. For linear dielectric materials with a relative dielectric permittivity \( \varepsilon_r \),

\[ U_e = \frac{1}{2} DE = 1/2 \varepsilon_r \varepsilon_0 E^2, \]

where \( \varepsilon_0 \) is the vacuum permittivity (=8.85 \times 10^{-12} \, \text{F/m}). Large dielectric permittivity can be obtained from ceramic materials. However, they generally suffer from relatively low breakdown strength. While polymers exhibit high breakdown strength, their low dielectric permittivity (e.g., <10) always limits the energy density. The composite approach capitalizes on the idea that the combination of inorganic materials of large permittivity with polymers of high breakdown strength may lead to a large energy storage capacity. Moreover, large interfacial areas in the composites containing nanometer scale fillers promote the exchange coupling effect through a dipolar interface layer and result in high polarization levels and dielectric responses.3 Compared to conventional ceramic materials, polymer-based dielectric materials also offer processing advantages including mechanical flexibility and ability to be molded into intricate configurations for electronic and electric devices with reduced volume and weight.

COMPOSITES BASED ON HYDROCARBON POLYMER MATRIX

One straightforward strategy to improve the dielectric permittivity of a polymer is the addition of inorganic fillers with high dielectric permittivity. Normally, ferroelectric ceramics, such as BaTiO3 (BT), Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT), or other ferroelectrics or relaxor ferroelectrics, possess a very large dielectric permittivity.5 It has been demonstrated that high dielectric permittivity ceramic fillers could greatly increase the dielectric properties of composites. For instance, a high dielectric permittivity of 49 was obtained at 100 Hz...
The effective dielectric permittivity of the nanocomposite has been estimated using various theoretical approaches. The Lichtenecker logarithmic rule is commonly used in a two-phase composite system to predict the effective dielectric permittivity based on the volume-fraction average:

$$\log \varepsilon = \phi_1 \log \varepsilon_1 + \phi_2 \log \varepsilon_2,$$

where $\phi_1$ and $\phi_2$ denote the volume fractions of ceramic fillers and polymer matrix, which have dielectric permittivities of $\varepsilon_1$ and $\varepsilon_2$, respectively.\(^7\) The effective dielectric permittivity of the binary composite given by the Bruggeman model is:

$$\phi_1 \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} + \phi_2 \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon} = 0,$$

which is based on a mean field approximation of spherical inclusions surrounded by polymer matrix.\(^8\) It has been shown that the effective dielectric constant predicted by the Bruggeman equation increases sharply for filler volume fractions above 20% and can be very high for ceramic particle loadings higher than 50 vol %. Additionally, the dielectric permittivity of the composites could be calculated according to the effective-medium theory (EMT) by averaging over the dielectric permittivity of the two constituents.\(^9\) An arbitrary fitting parameter was introduced in the model to account for the irregular morphology of the ceramic fillers. The experimental results of lead magnesium niobate-lead titanate/epoxy composites have been successfully fitted using the EMT model with less than 10% error.

A variety of chemical approaches have been developed to improve the dispersion of ceramic filler in polymer matrix. Polystyrene was directly grafted onto TiO₂ surface via the atom transfer radical polymerization (ATRP), which exhibited a dielectric constant enhancement of over three times that of bulk polystyrene.\(^10\) The high permittivity core lends high capacitance, while the flexible polystyrene shell endows the materials with good dispersability and film-form properties. As shown in Scheme 1, BT-PMMA (polymethyl methacrylate) nanocomposites were prepared via in situ ATRP of MMA from the nanoparticle surface.\(^11\) It was found that the nanocomposites showed an increased dielectric constant (~14 at 1 kHz), and the nanoparticles had no influence on the relaxation activation energy of PMMA matrix. Guo et al. prepared isotactic polypropylene-TiO₂ and BT nanocomposites via in situ-supported metallocene olefin polymerization process.\(^12\) The composites exhibited respectable permittivities (~6.1), high breakdown strength (~400 MV/m), and an estimated energy density of 9.4 J/cm³. It was speculated that, in a well-dispersed 0-3 composite, interfaces between the ceramic nanoparticle and polymer phases create effective electron scatters and transport centers, thus reducing the breakdown probability. Moreover, well-dispersed ceramic nanoparticles should block degradation tree growth and thus increase the long-term breakdown strength. The effect of shape of the nanoparticles on the effective permittivity has been further investigated and simulated.\(^13\) As illustrated in Scheme 2, aluminum oxide encapsulated high-permittivity BT, and ZrO₂ core-shell
nanoparticles were prepared via a layer-by-layer methyaluminoxane coating process and utilized as fillers in \textit{in situ}-prepared polypropylenes.\textsuperscript{14} The effective permittivity of the nanocomposites increases with the increase of the filler concentration, affording \( \varepsilon \) values as high as 6.2. It was found that the effective permittivity of the nanocomposites can be predicted by the Maxwell-Garnett formalism using the EMT for volume fraction of nanoparticles below 0.06. The incorporated moderate permittivity of the \( \text{Al}_2\text{O}_3 \) layer greatly suppressed leakage currents and decreased the dielectric loss of the composite. Recently, diblock poly(styrene-co-vinylbenzylchloride) was utilized as shielding layers on BT particles to enhance compatibility between the filler and polystyrene matrix.\textsuperscript{15} A large breakdown strength of up to 222 V/\( \mu \text{m} \) was achieved in the composites, leading to a noticeable energy density value of 9.7 J/cm\(^3\).

It is known that the introduction of specific functional groups at the particle/matrix interface can have profound effects on the electrical properties of nanocomposites. The influence of surface modification of \( \text{TiO}_2 \) nanoparticles on the short-term breakdown strength and space charge distribution of low-density polyethylene (LDPE) has been examined.\textsuperscript{16} As shown in Figure 1, it was found that the existence of polar groups such as \( N\)-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPS) onto the nanoparticle surface improved both the dielectric breakdown strength and space charge distribution as compared to LDPE filled with untreated nanoparticles, which were mainly due to enhanced electron scattering from the polar groups in AEAPS.

**COMPOSITES BASED ON FERROELECTRIC FLUOROPOLYMERS**

The hydrocarbon polymers used as matrices in the dielectric nanocomposites, including polyethylenes, poly(methyl methacrylate), epoxy resins, and polyimides, usually possess dielectric permittivities of \( \sim 2-5 \) that are significantly lower than their inorganic counterparts, thus severely limiting the energy density obtained in the polymer matrix and consequently, in the resulting nanocomposites. Generally, the energy density \( U_e \) of a diphasic composite is represented by the equation below:

\[
U_e = \phi_1 U_e^{(1)} + \phi_2 U_e^{(2)} + gU^{(3)},
\]

where \( \phi_1 \) and \( \phi_2 \) are volume fractions of the constituent dielectric materials in a composite and \( U_e^{(1)} \) and \( U_e^{(2)} \) are their corresponding energy densities, \( U^{(3)} \) is the energy density associated with interface effects, and \( g \) is proportional to the interfacial area—either a positive or negative
contribution to energy density. Therefore, it is important to have high energy densities from both phases in order for the nanocomposite to exhibit considerable energy density.

Poly(vinylidene fluoride) (PVDF)-based ferroelectric polymers exhibit large spontaneous polarization and high dielectric constants (\(\varepsilon_r \approx 10\) at 1 kHz) because of the presence of highly electronegative fluorine on the polymer chains and the spontaneous alignment of C-F dipoles in the crystalline phases.\(^{17,18}\) Superior energy density (e.g., 17 \(\text{J/cm}^3\) at 600 MV) that far exceeds those of conventional dielectric materials, such as biaxially oriented polypropylene, has been obtained in a defect-modified PVDF-based copolymer.\(^9\) PVDF and its copolymers, such as poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] and poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)], have thus been utilized in the formation of the dielectric nanocomposites.

**Ferroelectric Polymer Composites Containing Conductive Fillers**

It is known that the dielectric constant \((k)\) of composites can be greatly improved by adding conductive or semiconductive fillers in the insulator matrix as the volume fraction \(f\) of the fillers increases to the vicinity of the percolation threshold \(f_c\). \(k\) of the composites can be described by the well-known power law

\[
\frac{k}{k_m} \approx \left| f_c - f \right|^{-s},
\]

where \(k_m\) is the dielectric constant of the polymer matrix and \(s\) is an exponent of about 1. Using this strategy, the dielectric constant of composites can be increased to tens or even hundreds times the polymer matrix.\(^{20}\) For instance, tetrameric Cu-phthalocyanine was shown to possess a very high apparent dielectric constant \(\varepsilon_r = 10^4 - 10^5\) due to a nomadic polarization mechanism.\(^4\) Its polymer blends or grafted polymers with P(VDF-TrFE) exhibited large \(\varepsilon_r\) value.

---

**FIGURE 1** Weibull plots of dielectric breakdown strength of neat LDPE, LDPE filled with as-received TiO\(_2\) nanoparticles (AR-TiO\(_2\)/LDPE), and LDPE filled with AEAPS-coated TiO\(_2\) nanoparticles (AEAPS-TiO\(_2\)/LDPE). From Ma et al., Nanotechnology, 2005, 16, 724–731, © IOP Publishing Ltd, reproduced by permission.

**FIGURE 2** Effective dielectric constant of PVDF/xGnP nanocomposites as a function of the xGnP volume fraction, measured at 1000 Hz and room temperature. Inset (a) shows the best fits of the conductivity to the power law. Inset (b) shows the loss tangent of PVDF/xGnP nanocomposites as a function of xGnP volume fraction. From He et al., Adv. Mater., 2009, 21, 710-715, © John Wiley & Sons, Inc., reproduced by permission.
of 35–50 with 25–40 wt % loadings at 10 kHz.\textsuperscript{21} The dielectric constant of the Ni-PVDF composites with $f_{Ni}$ can reach about 400 and possess a weak frequency and temperature dependence.\textsuperscript{22} The incorporation of CCTO into P(VDF-TrFE) led to 0-3 composites with a dielectric constant of 610 at room temperature and 100 Hz, which was attributed to the heterogeneous relaxation in addition to the semiconductive nature of the fillers.\textsuperscript{23} Dang et al. fabricated the PVDF/carbon nanotube composites, with a percolation threshold of 8 vol %, possessing a dielectric constant of 600 and a dielectric loss (\tan d) of 2 at 1 kHz.\textsuperscript{24} For poly(vinylidene fluoride-trifluoroethylene-ter-chlorofluoroethylene) P(VDF-TrFE-CFE)/carbon nanotube composites, the dielectric constant increased from 57 to 102 (\tan d/C payoff.0.36) at 100 Hz by inclusion of only 2 wt % (1.2 vol %) carbon nanotube.\textsuperscript{25} A dielectric constant as high as 56 was observed in PVDF/acylene-black composites, when the acetylene-black concentration was in the neighborhood of the percolation threshold (about 1.3 vol %).\textsuperscript{26} More recently, Fan and coworkers reported that, for the composites of PVDF/exfoliated graphite nanplates (xGnP) fabricated by a solution-cast and hot-pressing method, a high dielectric constant of more than 200 and 2,700 could be obtained near the percolation threshold (1.01 vol %) at 100 and 1,000 Hz, respectively, which are 20 and 270 times higher than that of the PVDF matrix (Fig. 2).\textsuperscript{27} The giant increment in the dielectric permittivity was explained by the combination of the microcapacitance-structure model and the Maxwell-Wagner-Sillars (MWS) effect.

One issue of these composites is the increase of dielectric loss simultaneously with the dielectric constant. When the composition of composites approaches the percolation threshold, the dielectric loss is normally very high and the breakdown strength is also significantly reduced. Since the dielectric strength of this class of composites remains unclear, the usefulness of this approach for high energy density capacitors requires further study.

**Ferroelectric Polymer Composites Containing Surface-Functionalized Fillers**

Dispersion of inorganic fillers in the ferroelectric polymers is always problematic because of the low surface energy of the fluoropolymers. The agglomeration of the ceramic dopants gives rise to electron conduction for a high dielectric loss and undesirable porosity for dielectric failure at much lower fields. It has been shown by Perry et al. that phosphonic acid surface-modified BT nanoparticles yielded well-dispersed P(VDF-HFP) composites.\textsuperscript{28} The effective permittivity of nanocomposites with low volume fractions (<50%) was in good agreement with standard theoretical models, with a maximum relative permittivity of 35. However, as shown in Figure 3, for nanoparticle volume fractions of greater than 50%, the effective permittivity was observed to decrease with increasing nanoparticle volume fraction, and this was correlated with an increase in porosity of the spin-coated nanocomposite films. The dielectric breakdown strength was also found to decrease with increasing volume.

[FIGURE 3 Dielectric spectroscopy of each PFBPA-BT:P(VDF-HFP) nanocomposite from 20 Hz to 1 MHz: dielectric constant (a) and the loss tangent (b). The dielectric loss gradually increases with increasing frequency and it is mainly due to a resonance of the polymer host. From Kim et al., ACS Nano, 2009, 3, 2581-2592, © American Chemistry Society, reproduced by permission.]

[FIGURE 4 The breakdown strengths (failure probabilities: 63.2%) at each volume fraction as determined from the Weibull analysis. From Kim et al., ACS Nano, 2009, 3, 2581-2592, © American Chemistry Society, reproduced by permission.]
fraction of the BT nanoparticles, with an abrupt decrease observed around 10% and a gradual decrease for volume fractions of 20–50% (Fig. 4). The measured energy density at a field strength of 164 V/μm increased to a value of 3.2 J/cm³ as the nanoparticle volume fraction is increased to 50%, roughly in line with the trend of the permittivity.

The chemical functionalization of the BT nanoparticles with ethylene diamine moieties on the surface also rendered the particles a homogeneous distribution in the poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-CTFE)] and poly(vinylidene fluoride-ter-trifluoroethylene-ter-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE)] matrix.29 The dielectric permittivity increased steadily with the increase of modified BT content. The electrical energy density of the nanocomposites as a function of filler concentration is summarized in Figure 5. Clearly, the addition of modified BT nanoparticles into the polymers greatly increased the energy density from 1.9 J/cm³ of P(VDF-CTFE) to 3.7 J/cm³ of the composites containing 23 vol % BT nanoparticles at 150 MV/m. The dominant role of dielectric permittivity of the polymer matrix in determining the energy density of the nanocomposite has also been demonstrated. Titanate was used to modify the surface of BT nanoparticles to establish the crosslinking between BT particles and polymers.30 Microstructural analysis revealed that coated BT nanoparticles were uniformly dispersed in PVDF, which led to a large enhancement of the dielectric breakdown strength (up to 250 kV/mm) at the BT volume content of 7%. More recently, the dependences of the dielectric and ferroelectric properties of the PVDF/BT composites on the nanoparticle sizes were investigated systematically.31 The remanent polarization was found to increase as the size of BT particles increases from 25 to 500 nm. The dielectric constant of the composites exhibited a complex variation: it reached a maximum value in the composites with BT nano-

particle sizes of 80–100 nm and decreased again when the particle size is further reduced under 50 nm.

**Ferroelectric Polymer Composites with the Interfacial Effect**

From the energy storage point of view, inclusion of the nanoparticles with a permittivity of about hundreds and even thousands into the polymers, which generally possess a permittivity less than 10, might not be desirable for an appreciable increase in energy density. As the filler has a much greater permittivity than polymer matrix, most of the increase in effective dielectric permittivity comes through an increase in the average field in the polymer matrix with very little of the energy being stored in the high permittivity filler phase. Furthermore, the presence of a large contrast in permittivity between two phases gives rise to a highly inhomogeneous electric field and thus a significantly reduced effective breakdown strength of the composite.

It has been proposed recently that the presence of a large amount of interfaces in nanocomposites could be utilized to benefit the electrical and dielectric properties of the polymers. It is argued that the properties of the interfaces between the particles and the matrix, which will themselves be of nanometer dimensions, will have an increasing dominant role in determining dielectric performance as the particle size decreases.3 Tanaka et al. proposed a multicore model for the interfaces in the nanocomposites, in which the interfacial area consists of the transitional layer tightly bonded with polymer and nanoparticles, a bound layer about 2–9 nm, which is formed by a polymer chain strongly bonded to the first layer, and a third loose layers, which is a region loosely coupling the second layer.32 In addition, the diffuse Couy-Chapman layer is superimposed over the three layers. It was found that interface layers in the nanocomposites might be more conductive than the polymer matrix, which mitigated the space charge accumulation and field concentration by fast charge dissipation.

Zhang and coworkers demonstrated large enhancement in the electric energy density and electric displacement level in the nanocomposites of P(VDF-TrFE-CTFE) terpolymer/ZrO₂ nanoparticles.33 Through the interface effect, the presence of 1.6 vol % of ZrO₂ nanoparticles raised the maximum electric displacement D from 0.085 C/m² under 400 MV/m in the neat terpolymer to more than 0.11 C/m² under 300 MV/m in the nanocomposites.

The dielectric nanocomposites composed of P(VDF-TrFE-CTFE)34 and surface-functionalized TiO₂ nanoparticles with comparable dielectric permittivities (~40) and homogeneous nanoparticle dispersions were prepared.35 It was found that the presence of the nanoscale filler favors the formation of smaller crystalline domains and a higher degree of crystallinity in the polymer. In drastic contrast to their weak-field dielectric behavior, substantial enhancements in electric displacement and energy density at high electric fields have been demonstrated in the nanocomposites. As shown in Figure 6(a), for the composites with 10 vol % TiO₂, the energy density is 6.9 J/cm³ at 200 MV/m, which represents a
45% increase in comparison to the polymer matrix with an energy density of 4.7 J/cm³ at the same field. The existence of the nanoparticle/polymer interfaces in the nanocomposites was evidenced in the dependence of the dielectric properties on temperature shown in Figure 6(b). A shift of the dielectric relaxation peak toward a lower temperature and a reduced dielectric loss tangent are presumably indicative of interface polarization interaction and an increased trap density in the nanocomposites. The large interface area in the nanocomposites would produce the MWS interfacial polarization at low frequencies and/or leads to an ”interaction zone” with Gouy-Chapman diffuse layer, thereby greatly affecting polarization and dielectric responses of polymer matrix.

More recently, a new approach for the preparation of dielectric polymer nanocomposites was reported. As shown in Figure 7(a), the strategy included the synthesis of the ferroelectric polymers terminated with phosphonic acids and subsequent utilization of reactive end-groups of the polymer for directly coupling with oxide nanoparticles to yield the covalent-bonded nanocomposites. It was demonstrated that covalent assembly of polymer matrix and inorganic filler not only led to highly dispersed nanofillers without additional surface modification but also provided great stability and offered enhanced interfacial interactions for high polarization responses under the applied fields. More interestingly, the nanocomposites exhibit remarkable dielectric strengths without the usual penalty of sacrificing electric strength and greatly improved energy densities than the matrix. The energy density is 11.2 J/cm³ for P(VDF-CTFE) with 9.1 wt % ZrO₂ at 270 MV/m, which corresponds to a ~60% increase in comparison to the polymer matrix [Fig. 7(b)]. The improvement in the energy storage capability of the nanocomposites has been rationalized based on the changes of polymer microstructures and the rise of the electric displacement induced by the incorporated nanofillers.

**SUMMARY AND OUTLOOK**

The field of dielectric polymer nanocomposites has witnessed many exciting progress over the past several years, and the pace of progress has continued to accelerate. By judiciously selecting a combination of polymer matrix and nanoparticles, the dielectric properties can be tuned and the energy density has been greatly improved in the polymer nanocomposites compared to those of polymer matrix. Various methods have been developed to incorporate the ceramic fillers into polymer matrix in a controlled fashion. The optimization organic–inorganic interface via surface functionalization of ceramic nanoparticle affords excellent compatibility between the fillers and the polymer matrix and ensures uniform composite films even at higher filler concentrations, leading to high breakdown strength of the composites. High dielectric performance in the nanocomposites has been realized via the large enhancement in polarization response at high electric fields and changes in polymer microstructure induced by the nanofillers.

There is plenty room for further improvement as several issues remain to be addressed. Enhancing dielectric constant but retaining high dielectric breakdown and achieving low dielectric loss are the major challenges in this field. Currently, a high volume percentage of ceramic loading is required to significantly improve the dielectric constants of polymer nanocomposites. However, at such high volume contents, the mechanical properties of the composites will deteriorate and thus affect the processability of the thin films. The breakdown strength of the composites will also be reduced at high filler concentrations. Since the energy density scales quadratically with the applied field, the reduction in breakdown strength may negate any potential increase in energy density. The contribution from the polymer–ceramic interfaces can be exploited to improve the energy density of the composites by improvement of the breakdown strength or enhancement of polarization response, or both. However, the nature of the interfaces is still not well understood. Many questions, such as how the interfaces are related to the structures of the components and how the interfacial
properties change with the filler size and the applied electric field, need to be addressed by a focused effort extending all the way from theoretical modeling, to rational design and synthesis of hybrid structures with engineered interfaces, to in-depth dielectric characterization. An improved understanding of the role of ceramic fillers and interfaces on charge trapping, electron scattering and packing of polymer chains on the breakdown strength, and the high-field dielectric responses is central to development of next-generation dielectric polymer nanocomposites. A systematic study of the chemical structures of polymers and fillers, and size and morphology of fillers versus dielectric performance at high electric field has not yet been carried out. Manufacturing issues such as film processing, deposition of electrodes, and integration into module assemblies must also be researched. As a highly interdisciplinary field, the progress in polymer composites for capacitive energy storage is critically dependent on successful interactions across the boundaries of traditional disciplines and collaborative efforts from chemists, physicists, and engineers.

The authors gratefully acknowledge support from the Office of Naval Research and the National Science Foundation.

REFERENCES AND NOTES