Nanoparticle, Size, Shape, and Interfacial Effects on Leakage Current Density, Permittivity, and Breakdown Strength of Metal Oxide—Polyolefin Nanocomposites: Experiment and Theory

Neng Guo,† Sara A. DiBenedetto,† Pratyush Tewari,† Michael T. Lanagan,*‡ Mark A. Ratner,*‡ and Tobin J. Marks*‡

†Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60208-3113 and ‡Center for Dielectric Studies, Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802-4800

Received September 11, 2009. Revised Manuscript Received December 2, 2009

A series of 0–3 metal oxide—polyolefin nanocomposites are synthesized via in situ olefin polymerization, using the following single-site metallocene catalysts: C2-symmetric dichloro[rac-ethylbenzisodienyl]-zirconium(IV), Me2Si(BuN)(η5-C5Me5)TiCl2, and (η5-C5Me5)TiCl3 immobilized on methylaluminoxane (MAO)-treated BaTiO3, ZrO2, 3-mol %-yttria-stabilized zirconia, 8-mol %-yttria-stabilized zirconia, sphere-shaped TiO2 nanoparticles, and rod-shaped TiO2 nanoparticles. The resulting composite materials are structurally characterized via X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), 13C nuclear magnetic resonance (NMR) spectroscopy, and differential scanning calorimetry (DSC). TEM analysis shows that the nanoparticles are well-dispersed in the polymer matrix, with each individual nanoparticle surrounded by polymer. Electrical measurements reveal that most of these nanocomposites have leakage current densities of ~10−6–10−8 A/cm2; relative permittivities increase as the nanoparticle volume fraction increases, with measured values as high as 6.1. At the same volume fraction, rod-shaped TiO2 nanoparticle—isotactic polypropylene nanocomposites exhibit significantly greater permittivities than the corresponding sphere-shaped TiO2 nanoparticle—isotactic polypropylene nanocomposites. Effective medium theories fail to give a quantitative description of the capacitance behavior, but do aid substantially in interpreting the trends qualitatively. The energy storage densities of these nanocomposites are estimated to be as high as 9.4 J/cm3.

Introduction

Future pulsed-power and power electronic capacitors will require dielectric materials with ultimate energy storage densities of > 30 J/cm³, operating voltages of > 10 kV, and millisecond—microsecond charge/discharge times with reliable operation near the dielectric breakdown limit. Importantly, at 2 and 0.2 J/cm³, respectively, the operating characteristics of current-generation pulsed power and power electronic capacitors, which utilize either ceramic or polymer dielectric materials, remain significantly short of this goal. An order-of-magnitude improvement in energy density will require the development of dramatically different types of materials, which substantially increase intrinsic dielectric energy densities while reliably operating as close as possible to the dielectric breakdown limit. For simple linear response dielectric materials, the maximum energy density is defined in eq 1,

\[ U_e = \frac{1}{2} \epsilon_r \epsilon_0 E^2 \]  

(1)

where \( \epsilon_r \) is the relative dielectric permittivity, \( E \) the dielectric breakdown strength, and \( \epsilon_0 \) the vacuum permittivity (8.8542 × 10−12 F/m). Generally, metal oxides have large permittivities; however, they are limited by low breakdown fields. While organic materials (e.g., polymers) can provide high breakdown strengths, their generally modest permittivities have limited their application.

Recently, inorganic—polymer nanocomposite materials have attracted great interest, because of their potential for high energy densities. By integrating the complementary

*Authors to whom correspondence should be addressed. E-mail addresses: mxml46@psu.edu (M.T.L.), ratner@northwestern.edu (M.A.R.), and t-marks@northwestern.edu (T.J.M.).


properties of their constituents, such materials can simultaneously derive high permittivity from the inorganic inclusions and high breakdown strength, mechanical flexibility, facile processability, light weight, and tunability of the properties (polymer molecular weight, comonomer incorporation, viscoelastic properties, etc.) from the polymer host matrix. In addition, convincing theoretical arguments have been made suggesting that large inclusion-matrix interfacial areas should afford greater polarization levels, dielectric response, and breakdown strength.

Inorganic–polymer nanocomposites are typically prepared via mechanical blending, solution mixing, and in situ radical polymerization, and in situ nanoparticle synthesis. However, host-guest incompatibilities introduced in these synthetic approaches frequently result in nanoparticle aggregation and phase separation over large length scales, which is detrimental to the electrical properties of the composite. Covalent grafting of the polymer chains to inorganic nanoparticle surfaces has also proven promising, leading to more effective dispersion and enhanced electrical/mechanical properties; however, such processes may not be optimally cost-effective, nor may they be easily scaled up. Furthermore, the development of accurate theoretical models for the dielectric properties of the nanocomposite must be accompanied by a reliable experimental means to achieve nanoparticle deagglomeration.

In the huge industrial-scale heterogeneous or slurry olefin polymerization processes practiced today, SiO$_2$ is generally used as the catalyst support. Very large local hydrostatic pressures arising from the propagating polyolefin chains are known to effect extensive SiO$_2$ particle fracture and lead to SiO$_2$–polyolefin composites. Based on this observation, composite materials with enhanced mechanical properties have been synthesized via in situ polymerizations using filler surface-anchored Ziegler–Natta or metallocene polymerization catalysts. Therefore, we envisioned that processes mediated by rationally selected single-site metallocene catalysts supported on ferroelectric oxide nanoparticles might disrupt ubiquitous and problematic nanoparticle agglomeration to afford homogeneously dispersed nanoparticles within the matrix of a processable, high-strength commodity polymer, already used extensively in energy storage capacitors. Moreover, we envisioned that the methylaluminoxane (MAO) co-catalyst layer applied to the metal oxide nanoparticle surfaces would, after polymer workup under ambient conditions, serve as an effective precursor for a thin Al$_2$O$_3$ layer to moderate the large anticipated pressure.


polyolefin–ferroelectric permittivity contrast. If too large, such contrasts are associated with diminished breakdown strength and suppressed permittivity.18,19

In a brief preliminary communication, we reported evidence that high-energy-density BaTiO3− and TiO2− isotactic polypropylene nanocomposites could be prepared via in situ propylene polymerization mediated by anchoring/alkylating/activating C2-symmetric dichloro[ rac-ethylenbisindenyl]zirconium(IV) (EBIZrCl2) on the MAO-treated oxide nanoparticles (see Scheme 1).20 The resulting nanocomposites were determined to have relatively uniform nanoparticle dispersions and to support remarkably high projected energy storage densities—as high as 9.4 J/cm3, as determined from permittivity and dielectric breakdown measurements. In this contribution, we significantly extend the inorganic inclusion scope to include a broad variety of nanoparticle types, to investigate the effects of nanoparticle identity and shape on the electrical/dielectric properties of the resulting nanocomposites, and to compare the experimental results with theoretical predictions. We also extend the scope of metallocene polymerization catalysts (see Chart 1) and olefinic monomers, with the goal of achieving nanocomposites that have comparable or potentially greater processability and thermal stability. Here, we present a full discussion of the synthesis, microstructural and electrical characterization, and theoretical modeling of these nanocomposites. It will be seen that nanoparticle coating with MAO and subsequent in situ polymerization are crucial to achieving effective nanoparticle dispersion, and, simultaneously, high nanocomposite breakdown strengths (as high as 6.0 MV/cm) and high permittivities (as high as 6.1)
can be realized to achieve energy storage densities as high as 9.4 J/cm3.

Experimental Section

I. Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of O2 and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum line (10−5 Torr), or in a dinitrogen-filled MBraun glovebox with a high-capacity recirculator (<1 ppm O2 and H2O). Argon (Airgas, pre-purified), ethylene (Airgas, polymerization grade), and propylene (Matheson or Airgas, polymerization grade) were purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. Styrene (Sigma–Aldrich) was dried sequentially for a week over CaH2 and then triisobutylaluminum, and it was freshly vacuum-transferred prior to polymerization experiments. The monomer 1-octene (Sigma–Aldrich) was dried over CaH2 and was freshly vacuum-transferred prior to polymerization experiments. Toluene was dried using activated alumina and Q-5 columns, according to the method described by Grubbs,21 and it was additionally vacuum-transferred from Na/K alloy and stored in Teflon-valve sealed bulbs for polymerization experiments. Ba-TiO3 and TiO2 nanoparticles were kindly provided by Prof. Fatih Dogan (University of Missouri, Rolla) and Prof. Thomas Shront (Penn State University), respectively.20 ZrO2 nanoparticles were purchased from Sigma–Aldrich. The reagents 3-mol-%-yttria-stabilized zirconia (TZ3Y) and 8-mol-%-yttria-stabilized zirconia (TZ8Y) nanoparticles were purchased from Tosoh, Inc. TiO2 nanorods were purchased from Reade Advanced Materials (Riverside, RI). All of the nanoparticles were dried in a high vacuum line (10−5 Torr) at 80 °C overnight to remove the surface-bound water, which is known to affect the dielectric breakdown performance adversely.22 The deuterated

solvent 1,1,2,2-tetrachloroethane-d₂ was purchased from Cambridge Isotope Laboratories (≥99 at.% D) and was used as-received. Methylaluminoxane (MAO; Sigma–Aldrich) was purified by removing all the volatiles in vacuo from a 1 M solution in toluene. The reagents dichlororac-ethylbisindenylzirconium(IV) (EBiZrCl₂), and trichloropentamethylcyclopentadienyltin(IV) (C₅Me₅TiCl₄) were purchased from Sigma–Aldrich and used as-received. Me₆Si(2BuN)(η²-C₅Me₅)TiCl₂ (CGC-TiCl₂) was prepared according to published procedures.²³ n⁺-Si wafers (root-mean-square (rms) roughness of ∼0.5 nm) were obtained from Montco Silicon Tech (Spring City, PA), and aluminum substrates were purchased from McMaster–Carr (Chicago, IL); both were cleaned according to standard procedures.²⁴

II. Physical and Analytical Measurements. NMR spectra were recorded on a Varian Innova 400 spectrometer (FT 400 MHz, 1H; 100 MHz, ¹³C). Chemical shifts (δ) for ¹³C spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. ¹³C NMR assays of polymer microstructure were conducted in 1,1,2,2-tetrachloroethane-d₂ containing 0.05 M Cr(acac)₃ at 130 °C. Resonances were assigned according to the literature for isotactic polypropylene, poly(ethylene-co-1-octene), and syndiotactic polystyrene, respectively (see more below). Elemental analyses were performed by Midwest Microlabs, LLC (Indianapolis, IN). Inductively coupled plasma–optical emission spectroscopy (ICP-OES) analyses were performed by Galbraith Laboratories, Inc. (Nashville, TN). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku DMAX-A diffractometer with Ni-filtered Cu Kα radiation (λ = 1.54184 Å). Pristine ceramic nanoparticles and composite microstructures were examined with a FEI Quanta sFEG environmental scanning electron microscopy (SEM) system with an accelerating voltage of 30 kV. Transmission electron microscopy (TEM) was performed on a Hitachi Model H-8100 TEM system with an accelerating voltage of 200 kV. Samples for TEM imaging were prepared by dipping a TEM grid into a suspension of nanocomposite powder and left until the powder began to melt. Once in this phase, the slurry mixture became a fine slurry. The slurry was then attached to the high vacuum line. Upon stirring, the slurry mixture immediately became purple. The slurry mixture was again subjected to alternating sonication and vigorous stirring for 2 days with constant removal of evolving CH₄. Next, the nanoparticles were collected by filtration and washed with fresh toluene (50 mL × 4) to remove any residual MAO. Then, 200 mg of metalloocene catalyst EBiZrCl₂ and 50 mL of toluene were loaded in the flask containing the MAO-coated nanoparticles. The color of the nanoparticles immediately became purple. The slurry mixture was then subjected to alternating sonication and vigorous stirring through shadow masks that defined a series of different areas (0.030, 0.0225, 0.01, 0.005, and 0.0004 cm²) at 3 × 10⁻⁶ Torr (at 0.2–0.5 Å/s). Electrical properties of the films were characterized by two probe current–voltage (I–V) measurements using a Keithley Model 6430 Sub-Femtoamp Remote Source Meter, operated by a local LABVIEW program. Triaxial and low triboelectric noise coaxial cables were incorporated with the Keithley remote source meter and Signatone (Gilroy, CA) probe tip holders to minimize the noise level. All electrical measurements were performed under ambient conditions. For MIS devices, the leakage current densities (represented by the symbol J, given in units of A/cm²) were measured with positive/negative polarity applied to the gold electrode to ensure that the n⁺-Si substrate was operated in accumulation. A delay time of 1 s was incorporated into the source–delay–measure cycle to settle the source before recording currents. Capacitance measurements of the MIM and MIS structures were performed with a two-probe digital capacitance meter (Model 3000, GLK Instruments, San Diego, CA) at ±5 and 24 kHz. Several methods have been developed to measure the dielectric breakdown strength of polymer and nanocomposite films.₁⁴,₂⁵ In this study, various methods were examined (e.g., pull-down electrodes²⁵), and the two-probe method was used to collect the present data because the top gold electrodes had already been deposited for leakage current and capacitance measurements. The dielectric breakdown strength of the each type of composite film was measured in a Galden heat-transfer fluid bath at room temperature with a high-voltage amplifier (Model TREK 30/20A, TREK, Inc., Medina, NY) with a ramp rate of 1000 V/s.²⁶ The thicknesses of the dielectric films were measured with a Tencor P-10 step profilometer, and these thicknesses were used to calculate the dielectric constants and breakdown strengths of the films samples (see Table 2, presented later in this work).

III. Electrical Measurements. Metal–insulator–metal (MIM) or metal–insulator–semiconductor (MIS) devices for nanocomposite electrical measurements were fabricated by first doctor-blading nanocomposite films onto aluminum (MIM) or n⁺-Si (MIS) substrates, followed by vacuum-depositing top gold electrodes through shadow masks. Specifically, a clean substrate was placed on a hot plate heated to just below the polymer–nanocomposite melting point. A small amount of the polymer nanocomposite powder was placed in the center of the substrate and left until the powder began to melt. Once in this phase, the polymer nanocomposite is spread over the center of the substrate using a razor blade. The sample was removed from the heat, cooled, and then pressed in a benchtop press to ensure uniform film thicknesses and smooth surfaces. Gold electrodes 500 Å thick were vacuum-deposited directly on the films

| Table 1. XRD Linewidth Analysis Results for the Oxide–Polypropylene Nanocomposites |
|-----------------|-----------|-------------------|-------------------|
| Powder Type     | 2θ (deg) | full width at half maximum (°) | Crystallite size (L nm) |
| BaTiO₃          | 31.412   | 0.254             | 35.6              |
| BaTiO₃ – polypropylene | 31.649   | 0.271             | 32.8              |
| TiO₂            | 25.360   | 0.317             | 27.1              |
| TiO₂ – polypropylene | 25.358   | 0.361             | 23.5              |

* Crystallite size (L) is calculated using the Scherrer equation: L = 0.91/λ (cos θ) where λ is the X-ray wavelength, θ is the diffraction angle, and θ is the Bragg angle.

stirring overnight. The nanoparticles were then collected by filtration and washed with fresh toluene until the toluene remained colorless. The nanoparticles were dried on the high-vacuum line overnight and stored in a sealed container in the glovebox at −40 °C in darkness.

V. Representative Synthesis of an Isotactic Polypropylene Nanocomposite via In Situ Propylene Polymerization. In the glovebox, a 250-mL round-bottom three-neck Morton flask, which had been dried at 160 °C overnight and equipped with a large magnetic stirring bar, was charged with 50 mL of dry toluene, 200 mg of functionalized nanoparticles, and 50 mg of MAO. The assembled flask was removed from the glovebox and the contents were subjected to sonication for 30 min with vigorous stirring. The flask was then attached to a high vacuum line (10⁻⁵ Torr), the catalyst slurry was freeze–pump–thaw degassed, equilibrated at the desired reaction temperature using an external bath, and saturated with 1.0 atm (pressure control using a mercury bubbler) of rigorously purified ethylene while being vigorously stirred. Next, 5 mL of freshly vacuum-transferred 1-octene was quickly injected into the rapidly stirred flask using a gas-tight syringe equipped with a flattened spraying needle. After a measured time interval, the polymerization was quenched by the addition of 5 mL of methanol, and the reaction mixture was then poured into 800 mL of methanol. The composite was allowed to fully precipitate overnight and was then collected by filtration, washed with fresh methanol, and dried on the high vacuum line overnight to constant weight.

VI. Representative Synthesis of a Poly(ethylene-co-1-octene) Nanocomposite via In Situ Ethylene + 1-Octene Copolymerization. In the glovebox, a 250-mL round-bottom three-neck Morton flask, which had been dried at 160 °C overnight and equipped with a large magnetic stirring bar, was charged with 50 mL of dry toluene, 200 mg of functionalized nanoparticles, and 50 mg of MAO. The assembled flask was removed from the glovebox and the contents were subjected to sonication for 30 min with vigorous stirring. The flask was then attached to a high vacuum line (10⁻⁵ Torr) and equilibrated at the desired reaction temperature using
an external bath. With 1.0 atm of rigorously purified argon bubbling (pressure control using a mercury bubbler), 5 mL of freshly vacuum-transferred styrene was quickly injected into the rapidly stirred flask using a gas-tight syringe equipped with a flattened spraying needle. After a measured time interval, the polymerization was quenched by the addition of 5 mL of methanol, and the reaction mixture was then poured into 800 mL of methanol. The composite was allowed to fully precipitate overnight and was then collected by filtration, washed with fresh methanol, and dried on the high vacuum line overnight to constant weight. Unfortunately, film fabrication of the composite powders into thin films for MIS electrical testing was unsuccessful, because of the high melting point of the polystyrene.

Results

The goal of this study was to synthesize well-dispersed polyolefin-based nanocomposite dielectric materials via in situ supported metallocene polymerization catalysis, to investigate the effects of matrix polymer and nanoparticle identities, loading, and shape on the electrical/dielectric properties of the resulting nanocomposites, and to compare the experimental findings with theoretical calculations. In the first part of the Results section, we demonstrate that diverse polyolefin nanocomposites can be synthesized from a variety of olefinic monomers and polymerization catalysts via in situ polymerization methodologies. Next, we discuss microstructural characterization of the nanocomposites, demonstrating that nanoparticle agglomeration can be satisfactorily disrupted with the present in situ synthetic approach. In the remaining parts of this section, we analyze, in detail, the effects of nanoparticle composition, volume fraction, and shape on the nanocomposite leakage current density, relative permittivity, breakdown strength, and ultimate energy storage density.

1. Synthesis of Metal Oxide–Polyolefin Nanocomposites. As one of the most commonly used polymers in large-scale power capacitors, isotactic polypropylene offers greater stiffness, lower shrinkage, and less deterioration of dielectric properties at higher temperatures than other types of polypropylene. Therefore, the C2-symmetric metallocene catalyst dichloro[rac-ethylidenbisindenyl]zirconium(IV) (EBIZrCl2), with demonstrated selectivity for highly isospecific olefin polymerization, was chosen for immobilization on the surfaces of MAO-treated metal oxide nanoparticles, to create metal oxide–isotactic polypropylene nanocomposites (recall Scheme 1).

The nanocomposites were characterized using a full complement of spectroscopic and analytical methodologies. XRD line width analyses using the Scherrer equation indicate that the microstructures and coherence lengths of the individual nanoparticles remain largely unchanged throughout the olefin polymerization/deagglomeration process (see Table 1). Solution-phase 13C nuclear magnetic resonance (NMR) spectroscopy (shown in Figure 1) indicates that the present polypropylenes are highly isotactic, as evidenced by the measured isotacticity index, [mmm] = 83%. The number-average molecular weights of the polypropylenes are estimated to be >18 000, based on the relative peak intensities of the repeat unit methyl peak versus the polymer-chain end methyl peak in the 13C NMR spectra. Differential scanning calorimetry (DSC) confirms the absence of extensive amorphous regions in the composites, because only isotactic polypropylene melting features (142–147 °C) are detected. Powder XRD data for the nanocomposites also reveal the presence of monoclinic α-phase crystalline isotactic polypropylene (2θ = 14.2°, 17.0°, 18.6°, and 21.8°). It is observed that the melting temperatures of the nanocomposites generally (and not surprisingly) increase as the nanoparticle loading increases (see Table 2, presented later in this work), which is reasonably due to attractive interactions between the nanoparticles and the crystalline regions of the isotactic polypropylene.

Linear low-density polyethylene (LLDPE) is another polymer that is widely used in power capacitors. Compared to isotactic polypropylene, the chain branching in the LLDPE affords better processability. Therefore, the sterically open constrained geometry catalyst Me2Si[(Bun)N(η5-C5Me4)TiCl2 (CGCTiCl2)35 was utilized to synthesize BaTiO3–LLDPE nanocomposites via in situ ethylene + 1-octene copolymerization. Figure 2 presents a representative solution-phase 13C NMR spectrum of the nanocomposite, with the 1-octene incorporation.

Figure 1. 13C NMR spectrum of an isotactic polypropylene BaTiO3 nanocomposite (100 MHz, CD2Cl2 solution, 130 °C).


level calculated to be 25.0 mol %.\(^{(36)}\) DSC measurements also confirm the formation of LLDPE, with a typical melting temperature of 125.3 °C.\(^{(34)}\) Syndiotactic polystyrene has greater heat resistance\(^{(37)}\) than isotactic polypropylene, which can only operate at <85 °C when incorporated into film capacitors.\(^{(17)}\) Employing the same protocol as that described for EBIZrCl\(_2\), the “half-metallocene” catalyst Cp*TiCl\(_3\)\(^{(37)}\) was immobilized on MAO-treated ZrO\(_2\) nanoparticles. Subsequent in situ styrene polymerization affords ZrO\(_2\)-syndiotactic polystyrene nanocomposites. A representative solution-phase \(^{13}\)C NMR spectrum is shown in Figure 3. The characteristic single resonance near δ = 145.6 ppm for the ipso phenyl carbon atom confirms the formation of syndiotactic polystyrene, which is further substantiated by the distinctive melting temperature (267.0 °C) measured by DSC.\(^{(37)}\)

**II. Nanocomposite Microstructure.** During the course of an in situ metallocene-catalyzed polymerization process, the polymer chains that propagate at the nanoparticle-immobilized metallocene catalytic centers are expected to create large local hydrostatic pressures,\(^{(12)}\) which, when combined with the sonication in toluene during the metallocene catalyst immobilization on the nanoparticles, aids in disrupting the nanoparticle agglomeration. This process is confirmed by the comparative electron microscopic characterization of the as-received pristine nanoparticles and the resulting nanocomposites. As depicted in Figure S1 (in the Supporting Information), as well as Figures 4–6, the as-received pristine nanoparticles show very high levels of agglomeration; however, in the polyolefin nanocomposites, the agglomeration of the nanoparticles is significantly disrupted, with each individual nanoparticle being surrounded by a layer of matrix polymer.

Nanocomposites with poly(ethylene-co-1-octene) or poly styrene were not characterized further with SEM and TEM, nor in films for MIS devices, because these composites could not be fabricated into uniform, smooth films, using a variety of techniques. Therefore, the remainder of the Results section focuses on: (i) the electrical characterization of the isotactic polypropylene nanocomposites and (ii) the effects of using nanoparticles that have different permittivities and shapes.

**III. Nanocomposite Permittivity.** Metal–insulator–metal (MIM) and metal–insulator–semiconductor (MIS) devices for nanocomposite electrical measurements were fabricated by first doctor-blading nanocomposite films onto aluminum or n\(^+\) Si substrates, followed by thorough drying, then vacuum-depositing top gold electrodes through shadow masks. Capacitances were measured at 10 kHz, which is a sufficiently high frequency to avoid the complications that arise from ion conduction and interfacial polarization effects.\(^{(38)}\) After the film capacitance and (thickness) was measured at multiple locations on the nanocomposite film specimens with different size electrode areas (see Figure 7), the relative permittivity (\(\varepsilon_r\)) of the nanocomposite was calculated from eq 2,

\[
C = \frac{\varepsilon_0 \varepsilon_r A}{d}
\]

where C is the capacitance, A the electrode area, \(\varepsilon_0\) the permittivity of a vacuum (8.8542 × 10\(^{-12}\) F/m), and \(d\) the thickness of the nanocomposite film. Note that dielectric loss is another important property of the nanocomposite materials, which will be the subject of a separate dielectric spectroscopic study.\(^{(43)}\) Figure 7 shows a representative plot capacitance versus electrode area, the linearity of which indicates the good dielectric uniformity of the nanocomposite film.

Table 2 summarizes the permittivity data for the present nanocomposites. As the nanoparticle loading increases, the relative permittivity of the nanocomposites also increases, as predicted by the effective medium approximation (see more discussion below).\(^{(39)}\) More interestingly, at the same volume fraction, rod-shaped TiO\(_2\)–polypropylene nanocomposites exhibit significantly greater relative permittivities than those prepared with sphere-shaped TiO\(_2\) nanoparticles (compare entries 1–4 versus entries 11–13 in Table 2) under identical reaction conditions. This shape effect is argued to reflect the different depolarization factors for different inclusion particle geometries, according to the Maxwell–Garnett (MG) and Polder–Van Santen (PVS) effective medium models (see further discussion below).


IV. Permittivity, Breakdown Strength Measurements, and Leakage Current Density. In the preliminary communication of this work, we reported that anchored metalloocene-catalyzed in situ polymerization is a promising method to achieve well-dispersed ferroelectric nanoparticles in a polymer matrix. We speculate that, in a well-dispersed nanoparticle composite, interfaces between the ceramic nanoparticles and polymer phases create effective electron scatterers and trapping centers, thus reducing the breakdown probability (see more in the Discussion section). Recent dielectric characterization studies have shown that polymer structural relaxations and dipolar trap states are strongly influenced by the polymer/oxide interface. Moreover, well-dispersed ceramic nanoparticles should block degradation tree growth and thus increase the long-term breakdown strength. Here, we employ different metal oxide particles of varying permittivity for the enhancement of composite permittivity properties. In addition, all of the nanoparticles used in this study were coated with MAO.
as part of the polymerization process, and, as a result of this treatment, the nanoparticles have a thin Al2O3 ($\varepsilon_r \approx 10$) layer created by ambient exposure of the MAO-coated nanoparticles. This is anticipated to benefit the breakdown stability and permittivity enhancement by creating a graded permittivity decrease and reduced field contrast between the nanoparticles and the polymer. As one example, the high-permittivity BaTiO3–PP composites have a materials permittivity ratio of 1200:2.3, and ICP-OES analysis indicates that the estimated Al2O3 coating thickness on BaTiO3 is $\sim 1$ nm, creating a gradient of permittivities (1200:10:2.3). In the present modeling study (see discussion below), we neglect the $\sim 1$-nm-thick Al2O3 layer; however, we are currently investigating the effects of varying the Al2O3 layer thickness, both in conjunction with electrical measurements and with effective medium modeling.43

By varying the nanoparticle identity, we can investigate a range of permittivities to assess possible correlations with composite dielectric breakdown strength and effective nanocomposite permittivity. For example, a large permittivity metal oxide (such as BaTiO3) should afford greater increases in effective composite permittivity, as well as decreased breakdown strength, as can be seen by rearranging $U = 0.5\varepsilon_r\varepsilon_0E_r^2$ for $E_r^{1.7b,44}$ Because ZrO2 has a lower permittivity ($\sim 18-34$, depending on the yttria content)45 than TiO246 and BaTiO3,47 it is anticipated that the resulting polymer nanocomposites will exhibit larger intrinsic breakdown strengths and potentially enhanced energy storage densities. In the present study, it is observed that, at low nanoparticle loadings, the yttria-stabilized ZrO2$-$ and ZrO2$-$polypropylene nanocomposite films exhibit somewhat lower permittivities than neat polypropylene (see data given in Table 2), despite the fact that the permittivities do increase as the nanoparticle loadings increase. This result is most likely due to the significant film porosity visible during sample fabrication,\textsuperscript{2a,48} and, for this reason, Figure 8 shows only the ZrO2 nanocomposite effective permittivities for comparison to the other types of composites. Note that breakdown field strengths are known to be dependent on a variety of experimental conditions,\textsuperscript{49} and an exhaustive statistical analysis\textsuperscript{50} is required to make precise engineering-level comparisons between different nanoparticle–polymer composite films.

Interestingly, the present data show that the largest effective permittivities at low volume fractions are measured for polymer composites that have rod-shaped TiO2 nanoparticle inclusions, and not for composites that have the larger-permittivity BaTiO3 nanoparticles. This may be explained by the greater degree of electric field exclusion that arises from the rod-shaped inclusions (see discussion below of the permittivity, in terms of effective medium models).\textsuperscript{51} In addition, the rod-shaped TiO2 composite films have significantly lower breakdown fields than the corresponding sphere-shaped TiO2-, BaTiO3-, and ZrO2-based polypropylene nanocomposites, which might be expected, because enhanced localized electric field around the TiO2 nanorods facilitates increased charge injection. Moreover, the high aspect ratios of the TiO2 nanorods are more likely to approach the permittivity, relative to nanoparticle volume fraction and composition. Note that the effective permittivity of pristine isotactic polypropylene is $\sim 2.3$.

(43) Li, Z.; Fredin, L.; Lanagan, M. T.; Ratner, M. A.; Marks, T. J., manuscript in preparation.
The leakage current densities of the nanocomposite percolation at lower volume fractions, thus creating enhanced conduction pathways. Nevertheless, the range of measured breakdown voltages (fields) of the present nanocomposites is impressive (3–10 kV (1–6 MV/cm), which is indicative that that metal oxide nanoparticle inclusion can significantly enhance polymer dielectric breakdown strengths (values of 0.4 MV/cm have been reported for films of iso-PP,52 and 6 MV/cm52 for iso-PP films impregnated with benzyltoluene).53 The corresponding projected energy storage densities of the present composites vary from ∼0.3 (ZrO2–iso-PP and TiO2–iso-PP) to ∼9.4 J/cm3 (BaTiO3–iso-PP), which rivals or exceeds those reported for conventional ceramic54 polymer,55 and composite2a,16,56 dielectrics. Energy density is related to the dielectric breakdown strength, which is a statistically based process. The energy densities for large-scale capacitors that are fabricated from these nanocomposites will ultimately be dependent on reducing defects.

The leakage current densities of the nanocomposite films prepared in this investigation (Jleakage, depicted in Figure 9) are generally within the range of 10−8–10−6 A/cm² at 100 V. As the nanoparticle loading increases, most of the present nanocomposites exhibit depressed Jleakage values (Figure 9a) initially, presumably reflecting modified charge transport and interruption of conduction pathways within the composite structure by the nanoparticle inclusions.57 However, at the highest nanoparticle loadings (∼0.07 volume fraction), which are far below the percolation threshold (∼32%44), the polyolefin nanocomposites exhibit significantly enhanced leakage current densities, possibly because of film-fabrication-induced anisotropic agglomeration.55,58 This current density pattern with increasing volume fraction (an initial decrease, followed by an increase in Jleakage) is most clear in the BaTiO3–iso-PP composites (green curve, Figure 9a). No obvious correlations between oxide permittivity and Jleakage are observed. For example, ZrO2 has the smallest permittivity, yet the ZrO2 polymer–nanoparticle composites (including the yttria-stabilized nanoparticles) have the largest leakage current densities over the entire volume fraction range (see Figure 9), which is most likely attributable to space-charge differences59 that occur in the different types of composites. Nonetheless, the leakage current densities remain relatively small (<10−5 A/cm², Figure 9b), despite the increased effective permittivities of the polymer composites.

Discussion

I. Nanocomposite Synthesis and Characterization. Traditionally, a major limitation in preparing inorganic metal oxide–polyolefin nanocomposites has been the general phase incompatibility between polar inorganic metal oxide inclusions and the nonpolar polymeric organic host materials. For example, ferroelectric metal oxides are highly hydrophilic, whereas isotactic polypropylene is highly hydrophobic. Simple admixing of the two constituents negligibly disrupts the extensive

References


nanoparticle agglomeration and does not overcome the micrometer-scale or greater phase separation, which can lead to local dielectric breakdown and degrade nanocomposite electrical properties. In contrast, the present supported-metallocene in situ polymerization approach minimizes these limitations by achieving homogeneous nanoscale dispersion of the metal oxide phase: each individual nanoparticle is surrounded by polymer chains that propagate in situ from the high-productivity surface-immobilized metallocenium catalyst centers, thereby affording significantly enhanced composite dielectric properties (energy densities as high as 9.4 J/cm³).

II. Function of the MAO Cocatalyst. In nanocomposites that have very large contrasts in relative permittivities between host and guest materials, large disparities in the electric fields within the constituent phases occur, thus preventing the simultaneous realization of maximum energy densities for both constituents. For the present nanocomposites, however, the largest achieved energy density (as high as 9.4 J/cm³) is observed for BaTiO₃–PP composites, which have the largest materials permittivity ratio of ~522:1. We reasonably speculate that the thin Al₂O₃ coating on the nanoparticles created by ambient exposure of the MAO co-catalyst coating acts as a dielectric buffer layer between the high-permittivity BaTiO₃ nanoparticles and the low-permittivity polypropylene (PP) matrix. In this way, the BaTiO₃ polarizability can be fully utilized for charge storage in this type of core–shell composite.

III. Effect of Nanoparticle Shape on Nanocomposite Permittivity. Experiment versus Theory. The most common effective medium models are derived for the simple case of a spherical dielectric inclusion embedded in a sphere of host material. However, most materials do not occur naturally as spheres; therefore, effective medium models for other inclusion shapes have been developed. Simple analytical solutions for the effective permittivity (εₜₐₑᶠᶠ) can only be achieved for ellipsoids, whereas all other shapes require numerical solutions. The polarization of the composite is a function of the inclusion geometry and orientation with respect to the applied field. The depolarization factors (Nₓ, Nᵧ, Nz) describe the extent to which the inclusion polarization is reduced, according to its shape and orientation along each semiaxis of the ellipsoid. The depolarization factors are calculated from integrals, e.g., eq 3.

\[ Nₓ = \frac{aₓa₂aₙ}{2} \int_{0}^{∞} \frac{1}{(s+aₓ²)(s+a₂²)(s+aₙ²)} ds \]  

where aₓ, a₂, and aₙ are the semiaxes of the ellipsoid. For spheres, all three depolarization factors are equal (1/3, 1/3, 1/3), and for ellipsoids (infinite needles) the depolarization factors are 0, 1/2, 1/2, respectively (1, 0, 0, respectively, for discs). For the case of spherical inclusions, the effective permittivities are estimated using the Maxwell–Garnett (MG) effective medium theory (eq 4), and for the case of randomly aligned ellipsoidal inclusions, the effective permittivities are estimated using the Polder–Van Santen (PVS) formalism (eq 5), where εₓ is the relative permittivity of the TiO₂ inclusions, εₓ is the relative permittivity of isotactic polypropylene, fₓ is the volume fraction of TiO₂, and the N_j represents the depolarization factors.

\[ ε_{eff} = \frac{ε_b + 2ε_b(f_x(ε_a - ε_b))}{ε_a + 2ε_b(ε_a - ε_b)} \]  

\[ ε_{eff} = ε_b + \frac{f_x}{3(ε_a - ε_b)} \sum_{j=x,y,z} \frac{ε_{eff} - N_j(ε_a - ε_b)}{ε_{eff}} \]  

Figure 10 shows that a substantial enhancement in εₜₐₑᶠᶠ is predicted for ellipsoidal inclusions, compared to spherical inclusions. The enhancement is clearly greatest for flat disklike and for needlelike shapes, because of their larger dipole moments (versus spherical shapes). These observations motivated the present experimental study of TiO₂–isotactic polypropylene nanocomposites with different nanoparticle inclusion shapes. Although the effective medium models are only qualitatively accurate for the sorts of nanocomposites discussed here (where the dielectric contrast between polymer and filler is large, and the inclusion sizes are small), they nevertheless can act as guides to understanding the capacitance trends. The experimental results comparing TiO₂ nanocomposites with spherical and ellipsoidal inclusions are plotted, along with the modeling predictions, in Figure 11. It can be seen that the composites that contain ellipsoidal...
inclusions have larger effective permittivities at lower volume loadings than composites that contain spherical inclusions. Remarkably, the effective permittivities for spherical inclusions rise very slowly over the range of volume fractions, exactly as the Maxwell–Garnett formalism predicts (see Figure 10). In marked contrast, the effective permittivity of the composites that have inclusions with ellipsoidal shapes increases considerably as the inclusion volume fraction increases, which, again, is consistent with the trend predicted for ellipsoidal inclusions using eq 5.19,51

These results demonstrate that the present method of in situ polymerization for nanocomposite synthesis is highly effective in disrupting nanoparticle agglomeration and, therefore, achieving both high storage capacities as well as relatively accurate modeling of the permittivities within a straightforward effective medium description. Future synthetic and modeling efforts will focus on the permittivity gradient established by the interfacial Al2O3 layer to manipulate and understand the interaction between the oxide nanoparticles and the polymer matrix.43,59

Conclusions

We have synthesized and microstructurally/electrically characterized a series of well-dispersed metal oxide–polyolefin nanocomposites via a scalable, in situ supported metallocene-catalyzed olefin polymerization process. This versatile, scalable approach offers effective control over composite composition. By straightforwardly varying the nanoparticle identity, shape, and the metallocene catalyst, a wide array of nanocomposites with desirable dielectric and mechanical properties can be catalytically synthesized in situ. Generally, the leakage current densities of these nanocomposites (J\text{leakage} \approx 10^{-6}−10^{-8} \text{ A/cm}^2 \text{ at 100 V}) initially decrease as the nanoparticle volume fraction increases to \sim 0.07, at which point J\text{leakage} begins to increase. The relative permittivities of the nanocomposites increase as the nanoparticle volume fraction increases. At the same inclusion loading, polypropylene nanocomposites with rod-shaped TiO\textsubscript{2} nanoparticles exhibit significantly greater relative permittivities than those with sphere-shaped TiO\textsubscript{2} nanoparticles, in agreement with our theoretical predictions. The energy storage densities of the BaTiO\textsubscript{3}–polypropylene nanocomposites are projected to be as high as 9.4 J/cm\textsuperscript{3}. To achieve higher energy storage densities, both the experimental and theoretical findings presented here suggest that rational selection of the identity and shape of the metal oxide nanoparticles and engineering of the nanoparticle–polymer interface are essential.

Acknowledgment. This research was supported by ONR MURI Program (N00014-05-1-0766), by DOE (86ER13511), and made use of Central Facilities supported by the MRSEC program of the National Science Foundation (DMR-0520513) at the Materials Research Center of Northwestern University. The SEM and TEM analyses were performed in the EPIC facility of the NUANCE Center at Northwestern University. The NUANCE Center is supported by NSF-NSEC, NSF-MRSEC, Keck Foundation, the State of Illinois, and Northwestern University. We thank Mr. M. Russell for assistance with the SEM measurements and Dr. A. Facchetti for helpful discussions.

Supporting Information Available: TEM images of the 6.7-vol %-BaTiO\textsubscript{3}–isoPP and 6.2-vol %-TiO\textsubscript{2}–isoPP nanocomposites. This material is available free of charge via the Internet at http://pubs.acs.org.