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Supported Metallocene Catalysis for In Situ Synthesis of High Energy Density Metal Oxide Nanocomposites

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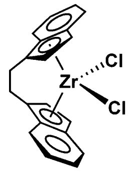
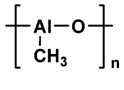
Future pulsed-power capacitors will require dielectric materials having very large energy densities, with operating voltages >10 kV, and millisecond−microsecond charge/discharge times with reliable operation near dielectric breakdown. Importantly, the operating characteristics of current state-of-the-art pulsed-power and power electronic capacitors, which utilize either ceramics or polymers as dielectric materials, fall significantly short of this goal.[1] Recently, inorganic−polymer nanocomposite materials have attracted intense interest due to their high energy density potential. By integrating complementary constituents, such materials can exhibit both high permittivity from the inorganic inclusions and high breakdown strength, mechanical flexibility, and facile processability from the polymer matrices.[2] Additionally, the large inclusion-matrix interfacial areas may afford higher polarization levels, dielectric response, and breakdown strength.[3]

Although inorganic−polymer nanocomposites can be prepared via mechanical blending,[4] solution mixing,[5] in situ radical polymerization,[6] and in situ nanoparticle synthesis,[7] host−guest incompatibilities usually result in nanoparticle aggregation and phase separation, which is detrimental to the electrical properties. Covalently grafting polymer chains to inorganic nanoparticle surfaces has also proven promising, leading to effective dispersion and enhanced properties.[8] In large-scale heterogeneous or slurry olefin polymerizations using SiO_2 as the catalyst support, very large local hydrostatic pressures arising from the growing polymer chains lead to SiO_2 particle fracture and to SiO_2−polyolefin composites.[9] We therefore envisioned that in situ polymerization using metallocene catalysts supported on ferroelectric oxide nanoparticles could disrupt nanoparticle agglomeration and lead to homogeneously dispersed ceramic nanoparticles within the matrix of a processable, high-strength polymer, already used extensively in energy storage capacitors.[10] In this contribution, we demonstrate that high energy density isotactic polypropylene−$BaTiO_3$ and TiO_2 nanocomposites can be prepared via in situ metallocene polymerization. Nanoparticle coating with methylaluminoxane (MAO) and subsequent in situ polymerization are crucial to achieving effective dispersion.



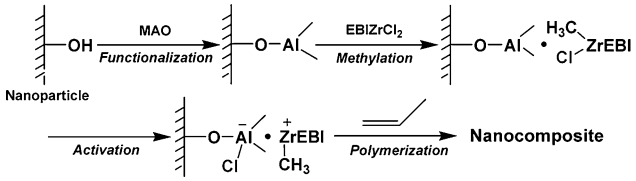
$EBIZrCl_2$



MAO

$BaTiO_3$ and TiO_2 40 nm nanoparticles are dried on a vacuum line to remove surface-bound water, known to adversely affect dielectric breakdown performance.[11] Nanocomposites are then synthesized via sequential nanoparticle MAO functionalization, catalyst immobilization/activation, and in situ isotactic propylene polymerization (Scheme 1). The first step is anchoring the MAO onto the nanoparticles via surface hydroxyl group reaction to form covalent Al−O bonds.[9] Anchored MAO functions as a cocatalyst to activate the metallocene, and in addition, the hydrophobic MAO functionalization helps disrupt, in combination with ultrasonication, hydrophilic nanoparticle agglomeration in the hydrophobic reaction medium. After washing away unbound MAO, the MAO-coated nanoparticles are subjected to reaction with the C_2-symmetric polymerization catalyst $EBIZrCl_2$ to afford surface-anchored, polymerization-active species. $EBIZrCl_2$-derived catalysts produce highly isotactic polypropylene, which, in conventional capacitors, affords enhanced mechanical and dielectric properties at elevated operating temperatures.[10] Subsequent in situ polymerization yields isotactic polypropylene−$BaTiO_3/TiO_2$ nanocomposites, the compositions of which can be tuned via the polymerization conditions.

Scheme 1. Synthesis of Isotactic Polypropylene−Metal Oxide Nanocomposites



The present nanocomposites were characterized by a full complement of spectroscopic and analytical methodologies. ^{13}C NMR shows that the polypropylenes are highly isotactic, as evidenced by the isotacticity index ([*mmmm*] = 83%, Figure 1).[12] DSC confirms the lack of large amorphous regions in the composites since only isotactic polypropylene melting features (130−150 °C)[13] are detected. X-ray diffraction (XRD) data for the nanocomposites reveal the coexistence of monoclinic α phase crystalline isotactic polypropylene (2θ = 14.2, 17.0, 18.6, and 21.8°)[14] and metal oxide nanoparticles [tetragonal $BaTiO_3$ (PDF No. 75-0462) and anatase TiO_2 (PDF No. 83-2243), respectively; e.g., Figure 2]. XRD line width analysis suggests that individual

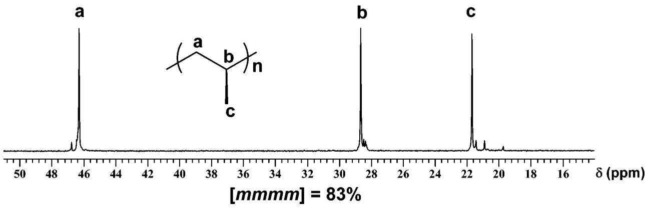


Figure 1. ^{13}C NMR spectrum of a polypropylene nanocomposite (100 MHz, $C_2D_2Cl_4$, 130 °C).

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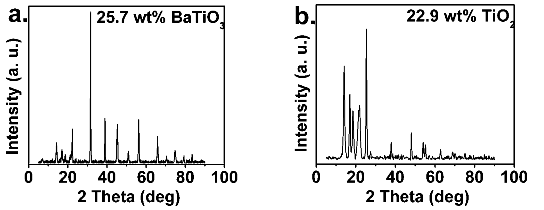

Figure 2. $\theta-2\theta$ X-ray powder diffraction patterns of (a) $BaTiO_3$− and (b) TiO_2−isotactic polypropylene nanocomposites.

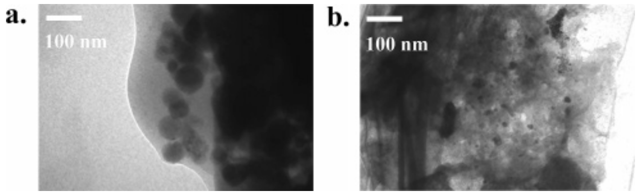

Figure 3. TEM images of (a) $BaTiO_3$− and (b) TiO_2−isotactic polypropylene nanocomposites.

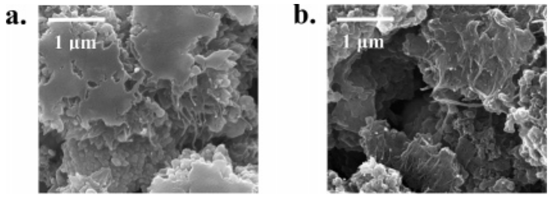

Figure 4. SEM images of (a) $BaTiO_3$− and (b) TiO_2−isotactic polypropylene nanocomposites.

nanoparticles remain largely intact upon deagglomeration.[15] Furthermore, TEM shows that the nanoparticles are homogeneously dispersed in the polypropylene matrices (Figure 3), while SEM images are consistent with polymer chain growth from the nanoparticles (Figure 4).

Nanocomposite films for electrical measurements were fabricated by doctor-blading. Leakage current measurements show the nanocomposites to be excellent insulators, as evidenced by very low leakage current densities ($\sim 10^{-6}$ to 10^{-9} A/cm^2 at 200 V).[15] Permittivities derived from capacitance measurements (as high as 6.1) agree with a Maxwell−Garnett effective medium approximation description.[15,16] That is, at low inorganic inclusion volume fractions, the relative permittivities of the nanocomposites should increase only moderately with increasing nanoparticle loading. The measured breakdown fields of the present nanocomposites are invariably ~4 MV/cm, indicating that metal oxide nanoparticle inclusion does not significantly decrease the dielectric breakdown strength. We speculate that, in a well-dispersed 0−3 composite, interfaces between the ceramic nanoparticles and polymer phases create effective electron scatterers and trapping centers, thus reducing the breakdown probability.[17] Moreover, well-dispersed ceramic nanoparticles should block degradation tree growth and thus increase the long-term breakdown strength.[18] Energy densities of the present nanocomposites are estimated to be as high as 9.4 J/cm^3, which rivals or exceeds those reported for conventional ceramic,[19] polymer,[20] and composite[21] dielectrics.

In conclusion, we have demonstrated that metal oxide−polymer nanocomposites can be catalytically synthesized via a scalable in situ supported metallocene olefin polymerization process. At relatively low nanoparticle volume fractions, the nanocomposites exhibit respectable permittivities and high breakdown strengths. This versatile approach offers effective control over composite composition and ready scalability. Further optimization of energy density is underway.

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Supporting Information Available: Detailed experimental procedures, TEM and SEM images of the pristine nanoparticles, and electrical characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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