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Improved polymer nanocomposite dielectric breakdown performance through barium titanate to epoxy interface control

Sasidhar Siddabattuni[a], Thomas P. Schuman[a,*], Fatih Dogan[b]

[a] Missouri University of Science and Technology (formerly the University of Missouri-Rolla), Chemistry Department, 400W. 11th Street, Rolla, MO 65409, USA
[b] Missouri University of Science and Technology, Materials Science and Engineering Department, 1400N. Bishop Avenue, Rolla, MO 65409, USA

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ABSTRACT

A composite approach to dielectric design has the potential to provide improved permittivity as well as high breakdown strength and thus afford greater electrical energy storage density. Interfacial coupling is an effective approach to improve the polymer-particle composite dielectric film resistance to charge flow and dielectric breakdown. A bi-functional interfacial coupling agent added to the inorganic oxide particles' surface assists dispersion into the thermosetting epoxy polymer matrix and upon composite cure reacts covalently with the polymer matrix. The composite then retains the glass transition temperature of pure polymer, provides a reduced Maxwell–Wagner relaxation of the polymer-particle composite, and attains a reduced sensitivity to dielectric breakdown compared to particle epoxy composites that lack interfacial coupling between the composite filler and polymer matrix. Besides an improved permittivity, the breakdown strength and thus energy density of a covalent interface nanoparticle barium titanate in epoxy composite dielectric film, at a 5 vol.% particle concentration, was significantly improved compared to a pure polymer dielectric film. The interfacially bonded, dielectric composite film had a permittivity ~6.3 and at a 30 μm thickness achieved a calculated energy density of 4.6 J/cm^3.

1. Introduction

Polymer/ceramic nanocomposites are promising dielectric materials for electrical energy storage applications as they combine the high dielectric constant of ceramic materials with a high dielectric breakdown strength [1–3]. Electrical energy density (U) of a linear dielectric material in the absence of loss is given by the equation $U = kE_b{}^2/2$, where k is the dielectric constant or permittivity of the material and E_b is the breakdown strength. Compared to conventional polymer/ceramic microcomposites, use of polymer/ceramic nanocomposites approach is appealing mainly for two reasons, large interfacial areas of nanocomposites [3,4] and possible miniaturization of dielectric composite films [1,5].

The addition of high surface energy ceramic particles into low surface energy polymer creates highly inhomogeneous electric fields at the interfaces that can conduct charge due to improper and inhomogeneous dispersion, resulting in reduced dielectric breakdown strength of the composites. Surfactants such as phosphate esters may be added to the polymer nanocomposites for improved quality of dispersion to increase the dielectric breakdown resistance compared to identical composites without dispersants [6]. Surface complexation of the ceramic particles before incorporating into polymer matrix using phosphonate, sulfonate, silane, and carboxylate based surface modifiers was recently tested by Schuman et al. and other researchers [6,7]. Phosphonic acids have been reported to bond to TiO_2, ZrO_2, and In–Sn oxide surfaces and are thought to couple through heterocondensation with metal hydroxides or surface metal (crystal-defect) ions [8–10].

Polymer nanocomposites prepared from surface modified ceramic particles with organo-phosphonates have resulted in improved dielectric breakdown resistance and energy storage densities. Examples include the embedding of high dielectric constant particles into poly(vinylidene difluoride) (PVDF), which increased the dielectric permittivity but reduced the dielectric loss and breakdown strengths compared to PVDF, resulted in an estimated energy density of about 6.1 J/cm^3 at 50 vol.% at a film thickness of about 3.84 μm [7]. The energy density was greater than the current state-of-the-art biaxially oriented polypropylene high energy density capacitors (1–3 J/cm^3).

The surface bond between the organophosphorous moiety and the metal oxide particle creates a stable, complexed organic oxide interface [6–10]. In producing a surface modified particle, only the particle surface is controlled by coupling agent, leaving the remaining polymer interface to be controlled by wetting and adsorption

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Abbreviations: BT, barium titanate; AEP, 2-aminoethyl dihydrogen phosphate; HP, hydrogen peroxide; DBS, dielectric breakdown strength.

* Corresponding author. Tel.: +1 5733416236.
E-mail address: tschuman@mst.edu (T.P. Schuman).

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interactions by the polymer chains, which is variable in structure [11]. What is less clear is if and how the surface modification alters charge carrier mobility and/or concentration of the particle surface as these defects could influence a dielectric breakdown event. Further, we seek to influence the bond between the coupling agent and the polymer matrix as well.

In general, commercial BT nanoparticles are aggregated and show poor dispersion in organic media. To improve the dispersion of BT nanoparticles in polymer matrix, surface modification is essential and is usually achieved by adsorptive surfactants or polymer coatings [12–14]. In the present work, we apply a bi-functional reagent, 2-aminoethyl dihydrogen phosphate (AEP) to modify the surface of barium titanate (BT) nanoparticles for dispersion and covalent reactivity within the epoxy polymer matrix. AEP not only bonds with particle surfaces, placing organic groups at the particle surface to assist with dispersion, but also reacts covalently with the epoxy polymer matrix to maintain crosslinking density near the particle surface.

However, we found that nano particulate BT lacked surface reactivity to the phosphate groups and thus was difficult to form chemical bonds with the surface modifying agents. We therefore synthesized surface hydroxyl groups on BT nanoparticles using aqueous hydrogen peroxide (HP) solution [15] so to improve the reactivity of BT nanoparticles towards a subsequent organophosphate treatment and composite interfacial strength against dielectric breakdown towards the overall goal of an improved energy storage density.

2. Experimental methods

In a typical surface modification reaction, nanoparticle BT (Sigma Aldrich, 30–50 nm particle size and 14 m^2/g average surface area) was dispersed in water (distilled and deionized) and degassed by sonication while under aspirator-reduced pressure for 15 min. AEP (Acros Organics)(∼6 wt.% of particle mass) was added to the BT filler dispersion and magnetically stirred at reflux for 5 h. The dispersion was then recovered by micro filtration followed by re-dispersion in fresh water and filtration, repeated twice. Surface activation of BT was achieved prior to surface modification by refluxing 10 g BT powder in 100 mL 30 wt.% HP solution (Acros Organics) for 2 h at 110 °C, which was cooled to 90 °C to add AEP and then magnetically stirred for an additional 2 h. The surface modified BT was then recovered by filtration followed by re-dispersion in fresh water and filtration, repeated twice. During surface activation of BT with HP solution, 2 h of reflux gave complete decomposition of HP with creation of hydroxyl groups on the surface of BT, based on the observation of the evolution of oxygen gas as by-product through bubbler. Commercially available BYK-w-9010 (Byk-Chemie, “a proprietary copolymer mixture with acidic groups”) was used as an adsorptive dispersant for comparison.

The powders, modified and unmodified, were analyzed by thermogravimetric analysis (TGA) and by X-ray photoelectron spectroscopy (XPS) [6,8,9]. TGA (Netzsch STA409) was used to measure the mass of organophosphate incorporated on the surface of particles. The number of phosphate groups located per surface area of particles may be estimated from the surface area per mass unmodified BT particles and mass organophosphate per mass particles [7–14]. Sample weight loss was measured from ambient to 800 °C at 10 °C min^{-1} in air.

An XPS (KRATOS model AXIS 165 XPS spectrometer) was utilized for determining the chemical composition of the particle surfaces using magnesium as the X-ray source [6]. Adventitious carbon for the C_{1s} orbital at a binding energy of 285.2 eV was used to correct for charging. XPS scans were performed on powder samples of 1 cm^2 mounted onto copper stubs with double-sided conductive adhesive tape and introduced into the UHV via a turbo-pumped antechamber.

Composite films were made by first dispersing particles into polyamide resin via a ball-milling process overnight (∼16–18 h). The polyamide resin used was a moderately low molecular weight, liquid, blend of the commercial Ancamide 2353 and Ancamine 2205 used at a 3:1 ratio and activated with 5 vol.% Ancamine K-54 that were each obtained from Air Products. A separate dispersant, the BYK-w-9010, was added only to a bare particle dispersion of BT in polyamide as an experimental control to compare a dispersed particle composite against a bare particle composite of no added dispersant (hence of poor dispersion) and against a self-dispersing (surface modified) particle, where the particle uses the bound surface groups to aid its dispersion. The ball-milled dispersion was sieved to remove the ball media into a clean, pre-weighed jar. Epoxy resin (Epon 828, Hexion), in amount stoichiometric to the amount of polyamine, was added to the dispersion and the uncured, liquid composite stirred for 5 min before degassing. Films of the uncured, liquid composite of 5 vol.% BT concentration were applied to freshly exposed, polished copper (Electronic grade 110 alloy, 0.8125 mm thick, #8 finish, obtained from McMaster Carr). Composites were allowed to initially cure overnight in a dust-free vented cabinet, followed by completing the polymer matrix crosslinking process by baking in a forced-air conventional oven at 80 °C for 24 h followed by 100 °C for 6 days. A 6 day cure was found necessary to remove all volatiles from the film and maximize breakdown strength.

Composite films were characterized by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) of the freeze-fractured cross section interfaces, ferroelectric testing, electrical impedance and dielectric breakdown strength. Film thicknesses were measured with a Mitutoyo 0293-340 micrometer and subtracting the thickness of the copper sheet.

Glass transition temperatures were assessed in a Perkin Elmer DSC after a preliminary thermal anneal stage (10 °C min^{-1}, from ambient to 100 °C, quenched to ambient temperature using liquid nitrogen) by scanning temperature from ambient to 150 °C versus an air-sealed pan. Glass transition temperatures are reported using the inflection point of the transition. Polarization as a function of electric field was measured with a ferroelectric tester (RT6000, Radiant Technology, NM, USA). The film morphology was imaged by using Hitachi S-4700 SEM after sputter coating the freeze fractured cross sections with a gold-palladium coating.

Parallel-plate capacitors were fabricated by depositing circular (31.67 mm^2) silver (Pelco® colloidal silver liquid, Ted Pella Inc.) top electrodes onto the nanocomposite thin films. Frequency-dependent capacitance was measured on a Solartron 1260 impedance analyzer connected with a Solartron 1296 dielectric interface (Solartron Analytical, Hampshire, England) at frequency range of 1 Hz to 1 MHz at 22 °C and from 0.01 Hz to 1 MHz at 100 °C with voltage amplitude of 1 V and analyzed by Zview® software. Reported relative dielectric constant used for energy density calculation was calculated according to capacitance measured at 10 kHz and at room temperature. Significant noise was observed at low frequencies. Thus, the 100 °C temperature measurements of dielectric constant and tan δ were performed to increase sample conductivity to improve signal to noise ratio especially in the low frequency range .

Dielectric breakdown strength measurements were made by applying D.C. voltage across the films using a Spellman SL 30 high voltage generator (Spellman High Voltage Electronics Corporation, New York, USA), with a fixed ramp rate of 200 V s^{-1} until the point of film failure. A pin electrode was applied by light spring tension to the surface of the composite, which served as the electrical ground. The Spellman