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Investigation of dielectric breakdown in silica-epoxy nanocomposites using designed interfaces

Michael Bell [a], Timothy Krentz [b], J. Keith Nelson [b], Linda Schadler [b], Ke Wu [c], Curt Breneman [c], Su Zhao [d], Henrik Hillborg [d], Brian Benicewicz [a,*]

[a] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29205, United States
[b] Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States
[c] Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, NY 12180, United States
[d] ABB AB, Corporate Research, Västerås SE-721 78, Sweden

GRAPHICAL ABSTRACT
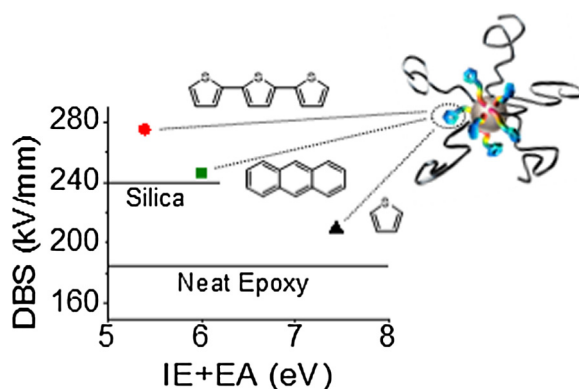
ABSTRACT

Adding nano-sized fillers to epoxy has proven to be an effective method for improving dielectric breakdown strength (DBS). Evidence suggests that dispersion state, as well as chemistry at the filler-matrix interface can play a crucial role in property enhancement. Herein we investigate the contribution of both filler dispersion and surface chemistry on the AC dielectric breakdown strength of silica-epoxy nanocomposites. Ligand engineering was used to synthesize bimodal ligands onto 15 nm silica nanoparticles consisting of long epoxy compatible, poly(glycidyl methacrylate) (PGMA) chains, and short, π-conjugated, electroactive surface ligands. Surface initiated RAFT polymerization was used to synthesize multiple graft densities of PGMA chains, ultimately controlling the dispersion of the filler. Thiophene, anthracene, and terthiophene were employed as π-conjugated surface ligands that act as electron traps to mitigate avalanche breakdown. Investigation of the synthesized multifunctional nanoparticles was effective in defining the maximum particle spacing or free space length (L_f) that still leads to property enhancement, as well as giving insight into the effects of varying the electronic nature of the molecules at the interface

on breakdown strength. Optimization of the investigated variables was shown to increase the AC dielectric breakdown strength of epoxy composites as much as 34% with only 2 wt% silica loading.

1. Introduction

Polymer based dielectrics have risen in popularity because of their low cost and processability compared to their inorganic counterparts. However, inorganic dielectrics remain superior in attaining dielectric properties [1]. The introduction of nano-sized inorganic fillers to polymers (nanodielectrics) can lead to improvements in permittivity, loss, voltage endurance, and dielectric breakdown strength compared to unfilled polymers [2–12]. Property enhancements found with nano-sized fillers are unseen or reversed with micron and larger sized fillers [11,13], and it has been shown that preserving the large surface area (interfacial region) that nanoparticles create is critical to attaining improved properties. The large surface area that contributes to property enhancement in nanodielectrics creates a challenge for maintaining dispersion, as it increases unfavorable interaction between the inorganic filler and organic matrix resulting in nano-filler agglomeration.

Ligand engineering has emerged as a critical tool for the evolution of property enhancements in polymer nanocomposites. The addition of carefully selected ligands to the filler surface offers tunability over interfacial, and ultimately, bulk properties of the composite. A common challenge addressed through ligand engineering is reducing the enthalpic penalty associated with incorporating inorganic fillers into an organic polymer matrix [14]. Ligands ranging from short organic molecules to polymer brushes have been employed to overcome this obstacle with varying success [15]. Multifunctional surface ligand engineering offers a unique strategy for introducing additional functionality into a composite by utilizing chemically distinct ligands on the same filler surface. A bimodal architecture generally utilizes one long and one short surface population. Previous publications have reported bimodal brushes on the nanoparticle surface where two populations of polymer chains are present [16–18]. This work will utilize a bimodal architecture consisting of long polymer brushes and small molecule surface ligands that introduces additional functionality separate from the long brush.

Thermochemical compatibility of isotropic nanoparticles in a polymer matrix was previously studied by Kumar et al. [19]. Through theoretical and experimental studies, it was determined that the dispersion of polystyrene grafted isotropic silica nanoparticles in polystyrene was influenced by the long and short range enthalpic interactions of the nanoparticles and the entropic displacement of polymer chains on the nanoparticle surface. It was found by tuning the parameters of grafted polymer graft density (σ) and the ratio of grafted chain length to matrix polymer chain length (N_g/N), a variety of anisotropic self-assembled structures could be achieved. This is because by altering graft density and molecular weight ratio, the effects of particle core-core attraction and grafted chain elasticity can be balanced. Multiple phases of filler dispersion including clusters, strings, and individually dispersed particles were realized by finely tuning the thermodynamic compatibility of the filler and matrix. Polymer graft densities of 0.01–0.1 ch/nm^2 were studied and results revealed that increasing the polymer graft density was effective at screening unfavorable particle core-core attraction resulting in improved particle dispersion.

Control over grafted chain density and chain length has been achieved using reversible addition fragmentation chain transfer (RAFT) polymerization. RAFT is a popular controlled radical polymerization (CRP) technique that allows for precise control over polymer molecular weight, architecture, and end group chemistry [20]. The control found with RAFT polymerization is due to the chain transfer agent, or CTA [21]. Surface initiated RAFT (SI-RAFT) polymerization utilizes a RAFT CTA covalently bound to a substrate surface as a means to outwardly grow polymer chains [22]. SI RAFT has become an integral part of ligand engineering because of the control it provides over a large selection of monomers, thus creating a toolbox of chemistries available for ligand design [21].

It is common practice to incorporate polycyclic aromatic compounds, known as voltage stabilizers, into polymers to improve dielectric performance. Investigation into the role of voltage stabilizers determined that π-conjugated small molecules acted as charge carrier traps, capturing free or "hot" electrons that are the precursors of avalanche breakdown [23]. The overall dielectric properties of the bulk polymer were shown to be altered depending on the electron nature of the additive [23,24]. Direct addition of voltage stabilizers can be problematic in that highly conjugated polycyclic compounds tend to crystallize in the polymer because they are insoluble [25,26]. Previous reports by our groups found that the direct addition of 9-anthracenemethanol to epoxy was detrimental to breakdown strength, the underlying cause most likely being a conductive pathway created across the polymer [3]. Addition of conjugated molecules to the nanoparticle surface offers a means to include electron trapping moieties at isolated regions of the composite without a conductive pathway. The large interfacial area of nanocomposites ensures a high probability of interaction between hot electrons and trapping moieties [4].

Schuman et al. presented a well correlated linear relationship of Hammett parameters to DBS for benzene derived functional groups on the surface of BaTiO$_3$ and TiO$_2$ in epoxy [8]. Much like Yamano's findings [23] regarding polycyclic voltage stabilizers, Schuman reported the addition of strong electron withdrawing groups (EWG) to the aromatic substituent to be most effective at improving overall DBS. Since Hammett parameters only define certain substituents on a benzene ring, it will be difficult to extend the utility of this model into further advanced systems. Predictions based on the sum of ionization energy (IE) and electron affinity (EA) could provide a much more generally applicable metric to predict DBS in surface modified composites [27]. Ionization energy and electron affinity describe the oxidation and reduction potential of a molecule, respectively. Koopman's theorem approximates IE and EA to corresponding HOMO and LUMO energies. The HOMO and LUMO levels of the small molecule surface ligands used in this work lie inside the band gap in the epoxy matrix. This leads to the introduction of spatially localized trap states for holes traveling in the valence band and electrons in the conduction band. The introduction of such traps in oil based insulations has been shown to lead to a reduction in hot carriers which decreases damage resulting in improved DBS [28].

In this material system, the literature indicates that the mode of breakdown is through electron avalanche processes [29]. This phenomenon has been described in detail in the literature [30–33]. In general, electron avalanches develop when an electron gains sufficient energy to lead to impact ionization and subsequent charge multiplication. Seitz's model assumes that failure occurs when an avalanche forms that is large enough that the population of electrons can gain sufficient energy from the field to lead to large scale