Technical Section

Technical Objectives
Nanodielectrics, typically consisting of nanoparticle or nanofiber filled polymers, have demonstrated significant improvements in electrical endurance, breakdown strength, dielectric constant, and energy storage properties. There is, however, a lack of consensus on what mechanisms lead to these outstanding properties, necessitating an empirical approach to developing new nanodielectric materials. However, to optimize and tailor the dielectric properties, a set of design rules must be developed based on a fundamental understanding of the role of the local electron trapping behavior, dielectric properties, and nanofiller dispersion. In turn, the nanofiller dispersion is critically dependent on the filler/matrix interface enthalpy and entropy. We are building on the hybrid materials informatics and finite element (MQSPR/FEA) approach we developed for predicting thermomechanical properties of spherical nanofilled polymers, and extending our work into the field of nanodielectrics. As part of this project, we are taking advantage of our ability to predict filler / matrix enthalpic interactions and particle dispersion, as well as build realistic 3D models of dispersion that include appropriate interphase regions. We plan to extend that to include predictions of the impact of interface entropy (following Pyramtisyn et al) on dispersion, and reconstruct 3D models of spherical and plate-like fillers. The models will include MQSPR predictions of the electron trapping, electron donating and dielectric properties of the interfacial regions and their role in controlling bulk dielectric properties such as breakdown strength, endurance strength, and dielectric constant. Therefore, the goal of this grant is to implement a fundamental Materials Informatics (MQSPR) approach, together with novel combinations of other computational methods (Hartree-Fock, DFT and FEA), to capture the nanoscopic interactions between polymers and particles, particle assembly, dispersion, and distribution at the microscale, percolation of both fillers
and interfacial properties, and predict (as well as to explain) the dielectric macroscopic properties for composites with complex geometries.

Technical Approach

Our first application of Materials Quantitative Structure-Property Relationships (MQSPR) to link disparate length (and time) scales was novel. In that approach, we begin by using the computational tools considered most appropriate for independently representing the properties of each length scale (ab initio DFT and semi-empirical quantum calculations for atomistic scale, molecular mechanics for nano-scale, and finite-element and continuum mechanics for micro-scale and bulk), the results of which were then linked to each other using heuristic models and validated against experiment to produce a modeling system capable of predicting the nano, micro, and macroscopic materials properties of novel nanocomposite materials. The relationships discovered during the scale-bridging process allowed some of the physics-based steps to be replaced by MQSPR models, therefore eliminating the need for some of the resource-intensive numerical calculations normally required during the process of engineering design. MQSPR models based on unique scale-dependent descriptors and non-linear machine learning methods were used to create mathematical relationships that correlate chemical structures of the filler and matrix with their surface energy properties, allowing us to predict the relative work of adhesion and work of spreading at the interface. Through careful experimental validation, we showed that we can create an analytical equation that then relates the work of adhesion to the filler dispersion. The resulting dispersion parameters were then used to build a 3D composite structure that was imported into a finite element code. We also developed an analytical expression relating the work of spreading to the change in interface relaxation spectra. This information is included in the finite element code allowing us to predict the thermomechanical properties of bulk polymer nanocomposites with spherical fillers. Currently, a user can invoke our web-based modeling program where they can choose a functionalized spherical filler with a specific surface chemistry, and a polymer matrix, and then be provided with qualitative predictions of dispersion and quantitative predictions of the thermomechanical properties of the resulting nanocomposite. The quality of the predictions compares favorably with macroscopic experimental results.

Our next step was to refine the thermomechanical approach and to predict the properties of nanodielectrics. This presented some new and interesting challenges. The first challenge involves computing the dielectric and electronic properties of the interfacial region around nanofiller particles, while taking proper account of the effects of nanoparticle decoration functional groups. We know this is critical because there are key examples of filler / matrix combinations that lead to unexpected increases (or decreases) in dielectric constant, most likely due to the dielectric behavior of the interface. We are taking advantage of this knowledge and creating nanodielectrics with nanofillers modified with polymer brushes of different sizes, chemistries, and graft densities (See Figure 1). This provides an opportunity to change the interface properties by placing polar molecules and electron trapping or electron donating groups near the nanoparticle surface while ensuring random particle dispersion and thus isolation of the interface regions. As part of the current work, we are invoking a modified version of our hybrid QM/MQSPR/FEA methods to predict the dielectric constant, breakdown mechanisms and electron trapping behavior of these new interfaces. A second challenge is in predicting the dispersion of these brush nanoparticles. Dispersion is significantly impacted by the brush graft density, molecular weight, and chemistry. Recent work (Langmuir paper, macromolecules paper) makes use of analytical expressions of polymer thermodynamics and the Hamaker constant to predict...
nanoparticle dispersion of grafted brush nanoparticles \(^1\), \(^2\) We are incorporating the properties and predictions of dispersion into a finite element tool (such as COMSOL Multiphysics) that we are utilizing to explore the dielectric properties and losses of proposed nanocomposite compositions. We are also developing a COMSOL method to provide at least qualitative predictions of changes in dielectric breakdown strength or endurance strength in novel nanocomposites. Thus we are working to accomplish the following goals:

(I) Incorporate the new methods for predicting dispersion based on the thermodynamics of polymer brushes and particle / particle Hamaker interactions into our modeling scheme

(II) Develop MQSPR methods (trained using DFT QM) for predicting the dielectric constant as well as electron trapping and donating properties both in the matrix (due to changes in mobility), and in designed interfaces with carefully chosen polar, electron trapping or electron donating molecules covalently linked to the nanoparticle.

(III) Develop a stochastic method to reconstruct the microstructure of the nanocomposites with fillers of different shape in the FEA modeling. The statistical information in the microscopic images is being processed and will be fed into a descriptor based reconstruction algorithm.

(IV) Develop FEA methods for predicting the frequency-dependent dielectric properties of nanocomposites, including their dielectric loss. Simulate the dynamic breakdown process in order to obtain the intrinsic breakdown strengths and endurance strengths of nanocomposite materials.

(V) Illustrate the scope and applicability of the hybrid MQSPR modeling system to design long/short brush nanocomposites with predicted, well-defined properties.

To achieve the goal of prospective nanocomposite property prediction and material design across scales, we proposed an informatics-based approach coupled with physics-based modeling and experimentation to develop computational methods that capture:

- **Pertinent local dielectric and electronic (electron capture and donating) properties,**
- **Nanoscopic thermodynamic interactions between polymers and particles, including distributions of particle assemblies, dispersion, and anisotropy of particle distributions at the microscale,**
- **Percolation of both fillers and interfacial properties, and**
- **Macroscopic properties.**

Our approach is twofold: First, we are using MQSPR modeling methods to develop a set of scale-bridging techniques (Figure 2) that relate chemical structure and filler morphology to the key properties at each length scale that control macroscopic properties. Then, building on our already-developed tools for building representative 3D models of nanofiller dispersion, we are developing methods to construct model composites for both spherical and plate-like fillers. Second, we are using FEA continuum methods to predict the dielectric properties and electric breakdown strengths of the nanocomposites. To accomplish the first part, we will apply MQSPR modeling methods and customized sets of descriptors to link the

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length scales and reduce the need for detailed calculations. For example, at the molecular level, we have already related filler and polymer chemical structure to filler/matrix interface enthalpy. We will now use MQSPR and a modified Pryamitsyn model (Langmuir and Macromolecules Schadler papers) to relate the graft density and molecular weight of the filler surface modifiers to calculate the entropy. We then construct new heuristics models that relate interface thermodynamics to filler dispersion (building off of current self-consistent theories). Additionally, we are developing a combination DFT QM and MQSPR to create models that can predict the dielectric constant of the interface region and its effect on the dielectric behavior of the composite. Using the predictions of local dielectric constant and electron trapping behavior as well as dispersion, we have built a COMSOL model to predict intrinsic breakdown strength, endurance strength, and dielectric constant and loss.

**MG Predicting Dielectric Permittivity of Polymer Composites**

![Diagram of MG Predicting Dielectric Permittivity of Polymer Composites](image)

Figure 2. Schematic illustrating the conceptual approach described in this work.

**Progress Statement Summary**

This section should be 1-2 paragraphs, text only and can also be used as your progress statement in section #5 of the website.

Immediately prior to the current period of work, we published a paper in Advanced Functional Materials that has attracted significant attention and has stimulated a great deal of discussion within the materials community. During the past year, all three PIs have given multiple invited talks based on this paper which outlines our framework for a hybrid MQSPR / FEA method capable of predicting the thermomechanical properties of polymer nanocomposites. These presentations often included significant aspects of our current work in hybrid MQSPR / FEA nanocomposite dielectric property modeling. This work also resulted in the predictive webtool that is illustrated in Figure 3. A new version of this web tool is available online at the following link: [http://reccr.chem.rpi.edu/polymerizer](http://reccr.chem.rpi.edu/polymerizer). Over the past year, the technology embedded in this tool has been enhanced, particularly in the prediction accuracy of the dispersion component of the surface energy, and its capabilities have been increased.
We are currently focused on four main thrusts:

1) Building a COMSOL API-enabled software package for modular dielectric spectroscopy analysis, including image characterization, descriptor-based structure reconstruction, as well as finite element analysis of dielectric properties. This method takes explicit structure geometry in FEA with filler-matrix interphase region depicted by a series of Debye relaxation terms, referred as Prony Series for dielectrics nanocomposites, in order to simulate frequency dependent dielectric behaviors.

2) Studying the electron-related property of functional groups and relates it to the breakdown strength enhancement of the polymer nanocomposites.

3) Implementing all analytical approaches for dielectric constant enhancement developed previously by other researchers.

4) Creating the experimental data needed for dual brush modified nanoparticle composites to validate the models and provide hypothesis for the physical mechanisms occurring during breakdown.

**Progress**

This section will describe the accomplishments in detail for the current Fiscal Year for the project.

**Introduction:**

Advances made during the last year of the project was based upon work done during the previous year, and on the results and tools created through our earlier ONR-supported project (N 000141-01-02-4-4) during which the framework for a hybrid MQSPR/physics-based modeling method for predicting the thermomechanical properties of polymer nanocomposites was designed and implemented as a predictive webtool as shown in Figure 3. A public version of the tool is available online at the following link: [http://reccr.chem.rpi.edu/polymerizer](http://reccr.chem.rpi.edu/polymerizer).

During the current phase of the project, the technology embedded in the polymerizer tool was enhanced, and its capabilities were increased. Additionally, new hybrid methods are being developed that allow the prediction of both the dielectric constant and intrinsic breakdown strength of organic polymer nanocomposites. In another phase of this project, the 3D distributions of nanofiller particles in polymer matrices predicted by polymerizer technology will be used to feed data and physical constants into the breakdown simulation algorithm, which will then allow prediction of these important design parameters for nanocomposite materials with specific brush types grown on the nanofillers. An important aspect of this work is the ability to model the aggregation behavior of “dual brush” multi-functionalized nanofillers with electrically-optimized charge traps (short brushes) as well as compatibility regions (long brushes).

A second major aspect of the current work includes developing a new approach in COMSOL that would allow (for the first time) the prediction of dielectric breakdown strength and high field endurance. This is a critical component for the practical application of nanocomposites as both insulators and capacitor dielectrics.
A third aspect involves the synthesis and testing of dual-brush nanocomposite systems. This will not only allow for “closing the loop” model optimization, but the development of appropriate synthetic technology will permit blind testing of the prediction algorithms to determine their ability to design polymer nanocomposite materials with specific mechanical and dielectric properties. The first sets of designed multifunctional nanocomposites have been synthesized and tested using procedures developed as part of this project.

**Computational Progress:**

To capitalize on the discoveries and developments made earlier in this project related to using combinations of MQSPR and physics-based models to predict the thermomechanical properties of nanocomposites (polymerizer), we have now extended this work both conceptually and practically to develop methods that use MQSPR, ABAQUS, COMSOL, DFT and stochastic breakdown theory together to not only predict the mechanical properties of proposed nanocomposites, but also their dielectric and breakdown behaviors. The modeling process also allows us to explore different hypotheses for how the presence of functionalized nanoparticles with specific functional groups and defined volume fractions can affect these properties.

1. Progress in hybrid MQSPR / Physics-based modeling of the breakdown strength of polymer nanocomposite

As observed in experiments performed in Dr. Schadler’s group, functional groups grafted on the nanoparticles were generally found to increase the breakdown strength of the resulting polymer nanocomposites. Since increasing dielectric breakdown strength may be a more efficient way of increasing the energy density of capacitor materials, the optimization of functional groups and brush structures is a key part of the research effort. At present, there is no well-accepted theory that describes this phenomenon. Frohlich’s electron avalanche theory describes a phenomenon in which scattered energy levels (electron traps) provide extra sinks to dissipate the energy of hot electrons and therefore increase the breakdown strength. A review by Ku et al shows that depending on the temperature, different mechanisms may be dominating and that electron avalanche is significant when the temperature is lower than the glass transition temperature. For the polymer matrix used in this study, the Tg is usually higher than the working temperature, however the electron avalanche theory requires parameters that are system-specific and difficult to determine a priori.

In studies of polymer and polymer nanocomposites, determination of the physical nature of charge traps and their values have been reported. Meunier and Quirke proposed that the electron trapping in polymer matrices was due to conformational and chemical defects, and also provided an expression for the depth of electron trapping: $E_{\text{trap}} = E_{A\text{defect}} - E_{A\text{reference}}$ where the EA means electron affinity which can be estimated by the energy of the LUMO according to Koopman’s theorem. However, they also point out that the depth of electron trapping due to conformational defects is quite shallow (~0.2 eV) compared to chemical defects. Tanaka proposed that the electron traps could be represented as the potential well caused by the difference in dielectric constant between the polymer matrix and the functionalized nanoparticles. This method provides another possible source of electron trapping, but does not consider graft functional groups and assumes that large particles have better electron trapping capability, which is not supported by experiments. In 2009, Tanaka proposed that electron trapping due to chemical defects could be estimated from molecular orbital analysis, which is similar to Meunier’s approach mentioned above. In general, it is believed that electron traps are much deeper for nanoparticles than for chemical or conformational defects.
In this study, we found that the charge equilibrium between nanoparticle functional groups and the polymer matrix may be a major factor. Even though the mechanism of polymer breakdown and the physical nature of electron traps are both not clear, the equilibrium between the charged polymer chain and charged grafted nanoparticles exists and should contribute to the restriction of free electrons and stabilization of the system. Therefore, we calculated energy differences of these equilibria and showed that a relationship between the material breakdown strength and the charge trap depth does exist.

**Figure 4. Dielectric Breakdown workflow.**

**Method**

**Theory**

It is generally believed that the breakdown phenomenon starts with electron intrusion, where a small amount of free electrons move into the bulk materials in the early stage and induce more free electrons. We propose that the electron can be trapped if there is lower energy level locally and therefore creates a higher need for energy input to induce secondary free electrons. Such process can be simply described as follows:

\[
\text{Charged Polymer} + \text{Neutral Particle} \rightarrow \text{Neutral Polymer} + \text{Charged Particle}
\]

As basic thermodynamics indicates, the equilibrium will lie to the right if the energy cost from charged polymer to neutral polymer is larger than that for charged particle to neutral particle. In short, the electron has a higher probability staying on the particles rather than in the matrix if the charged particles are more stable. For certain polymer matrices, the energy cost of the polymer is fixed. Consequently, the effect of functional groups can be simply estimated by calculating the energy cost in going from charged particles to neutral particles.
The other possibility is that the positive charge (hole) may play a similar role in such process. The same formula used above can also be applied here. The only difference is that the nanoparticle will not accept electrons from matrix, but to lose them to positive charged polymers.

In the two processes, the energy cost calculated can be estimated by the adiabatic electron affinity EA (from neutral to anion) and ionization energy IE (from neutral to cation). More negative EA indicates larger ability of accepting an electron and smaller EA indicates the molecule is easier to give an electron to the polymer matrix and trap a hole. Two assumptions are made: 1. The existence of the nanoparticles only leads to very small change on the conduction band energy of the polymer matrix. 2. The kinetic effect of the charge transfer between polymer and nanoparticles are small and transfer is quick, so that the thermodynamics are dominating over kinetics.

**Computation**

Direct quantum computation on the realistic grafted nanoparticles requires enormous resources and is practically infeasible for the study purposes, and methods to examine charged systems using periodic condition is still under development. In this study, we used functional groups with a Si(OH)₃ substrate to simulate the nanoparticles. In the preliminary study, we found that the existence of the silica substrate did not influence the electron affinity and ionization energy of the functional groups. Such a finding agrees with chemical intuition that the empty orbitals in silica all contribute to the higher level of virtual orbitals in the system. Therefore, the HOMO and LUMO orbitals are mostly localized on the organic functional groups. Accordingly, the quantum computation were done on Si(OH)₃ based functional groups.

Quantum computation was performed using Guassian09, where the cation, anion and neutral molecule initial geometries were first prepared using a PM3 theoretical model. Then, the first stage of optimization was performed using HF/6-31G*, and the resulting geometry and orbitals were used as the input to the second stage using B3lyp/6-31+G*. B3lyp shows good performance for the computation of radicals and results in only slight spin contamination. The zero-point-energy (ZPE) was also calculated, using a correction coefficient of 0.75, as recommended in the literature. The optimized structure was then used to calculate the electronic energy using B3lyp/6-311++G**. The final energies were calculated as the sum of the electronic energy and the corrected ZPE.

**Functional Groups**

Four functional groups from Dr. Schadler’s group and five from Siddabattuni’s paper were used in this study, and the structures and names used in this report are listed below. The Si(OH)₃ in each structure was used to represent the silica nanoparticle surface. In Siddabattuni’s paper, the actual nanoparticles were titanium dioxide. However, using several atoms to represent the structure of titanium dioxide is much harder than for silica due to the fact that the coordination number of Ti in the crystal is not 4 but 6. We here assume the TiO₂ has a similar effect on virtual orbitals as does silica, as mentioned above. As a preliminary test, we also use Si(OH)₃ to represent the nanoparticles. The third column lists the dielectric breakdown strength.
Figure 5. Structures of nanoparticle electron traps on silica.
Results

The comparison between HOMO and LUMO orbitals of the neutral monothiophene functional groups, and the HOMO orbitals of the corresponding positive charged and negative charged ion radicals are shown in Fig 6, clearly the orbitals involved in the charge transfer process are strongly localized on the functional group, rather than on the silica particles. Such an observation supports the idea that the electrons, at least in the early stage of electronic charging, should stay on the polymers and functional groups. The nanoparticles may not, in fact, contribute much effect in the presence of conjugated functional groups. The spin density distribution of the charged ion radicals also shows the same result. This concept is simplified because the surface defects of nanoparticles are not included. However, in the two studies, all functionalized nanoparticles showed a greater ability of increasing nanocomposite breakdown strength over that of bare nanoparticles. This indicates that surface defects may be a minor factor in such systems.

Quantum calculations on the electron affinity (EA) and ionization energy (IE) were first performed on the monothiophene and anthracene functional groups. Comparison were then made between hydrogen terminated functional groups with silica (Si(OH)$_3$) terminated ones. The EA for monothiophene with hydrogen terminated was found to be -0.38 eV, IE is 8.14 eV. EA for monothiophene terminated with silica was -0.43 eV and IE is 7.87 eV. EA for anthracene with hydrogen termination was -0.79 eV and IE 6.8 eV. EA for anthracene with silica terminated is -0.8 eV and IE is 6.8 eV. Values for hydrogen terminated functional groups are quite close to those with silica termination, which further supports the theory that the nanoparticle will not influence the charge equilibrium between polymer matrix and grafted nanoparticles, at least in the early stage.
A plot of the breakdown strength with $EA+IE$ is shown in Fig 7. A clear trend was found as expected: the larger the $EA+IE$, the smaller the breakdown strength. In experiments, anthracene and ferrocene were found to have the same breakdown strengths. This deviation should be attributed to the other minor factors include the grafting density differences, kinetic limits, process defects and so on. The value of $EA+IE$ is based on the assumption that electron trapping is as significant as hole trapping, which may not be the case in reality. But since only very few data points are available, to distinguish the importance of the two mechanisms is difficult for now. Based on Koopmans’ theorem, $EA$ can be approximated by LUMO energy and $IE$ is corresponding to the opposite of the HOMO value. Therefore $EA+IE$ can be actually approximated by the HOMO-LUMO gap. That is, if electron trapping and hole trapping is of equal importance, then functional groups with larger conjugated systems will give good performance. In general, polymers with large conjugated systems were found to have low breakdown strengths, but in polymer nanocomposites, smaller HOMO-LUOMO gaps may be a positive driving force.
Figure 7.

Fig 7 shows the plot of Siddabattuni’s data. In that paper, the Hammett parameter was found to be well related to the breakdown strength for the four benzene-derived functional groups (PP, APP, CPP, NPP). Since the Hammett parameter is only defined for certain substituents of the benzene ring, such correlation is difficult to utilize in more general cases and the physical meaning of such a correlation is also hard to interpret. In Fig 8, we see that CPP, NPP and AEP follow the same trend as found in the previous case, the outliers are the PP and APP, which are both largely overestimated by the computation. The reason could be due to the bad dispersion state of the samples. In their paper, PP and APP have much larger beta values from the Weibull distribution and average separation. Both indicate a bad dispersion. In the previous case, since bimodal nanoparticle was used, and the dispersion state was controlled, which was also verified by the closeness of beta values. Further analysis and modeling is needed and the effect of dispersion will be studied using a stochastic model with FEM.
Stochastic FEM models with statistically equivalent microstructures were used to examine the breakdown tree pattern simulated by our previously developed random field method. In order to get around the need for high computational power, statistically equivalent 2D microstructures were reconstructed for FEA to model the dispersion states using a method similar to our original hybrid MQSPR tool polymerizer.

In this approach, a descriptor-based 2D reconstruction algorithm was used to generate an artificial structure for breakdown analysis. Input parameters for this reconstruction include the side length of simulation domain (L), the volume fraction of filler in composite (VF), the nearest center distance (ncd), as well as aspect ratio (asp) distribution. The dispersion state of the composite structure can be varied by controlling these four parameters during the reconstruction process. We are currently focusing on converting the descriptor-based structure algorithm into a COMSOL routine to investigate the effect of dispersion on the breakdown pattern. Sample dispersion structure is shown in Figure 9.

Figure 8.
Conclusions - Breakdown

This study gives a feasible solution to predict the ability of grafted functional groups on increasing the polymer nanocomposite breakdown strength. We find that both the electron affinity and ionization potential are important, even though the comparison on importance of the two values can not be done with the data we have. Such method is not developed for accurate prediction, or to give a rigorous explanation of the material breakdown. In this study, we show that the charge equilibrium between polymer matrix and functional groups may be the major process for charge trapping, and therefore such relation can be utilized for the screening of better functional groups.

Future Plans – Breakdown

1. Determine the relative importance of electron trapping and hole trapping by adding more experimental data.
2. Utilizing the relation found in this study and look for functional groups with better performance.
3. Incorporate the model of calculating the charge trapping in a FEM stochastic model to provide more accurate prediction.

2. Development of an FEA Model for Predicting the Dielectric Relaxation Process in Polymer Nanocomposites

Dielectric polymer nanocomposites have been widely studied as promising candidates for devices in electrical energy storage and power transport, as they combine the advantages of both high dielectric constant of the inorganic fillers as well as the high breakdown strength of the polymer matrix. Besides, the nano-sized fillers results in a large amount of interfacial area between the polymer matrix and the fillers with altered properties which provide the composites with improved performance. An accurate prediction of the dielectric spectroscopy of the composites is of great value in order to provide guideline for design of the dielectric polymer nanocomposites.
Homogenization models have been previously developed to predict the dielectric spectroscopy with parameters that qualitatively describe composite structure. For example, Maxwell-Garnett and Bruggemen models use simple mixing rule to directly calculate composite dielectric constant with assumption of very low filler loading. Power law and Hashin-Shtrikman models involve additional terms in parametric prediction of the estimated dielectric permittivity. More recent models, such as Vo-Shi and Todd-Shi models, also take into account of filler-matrix interphase layer into the prediction of dielectric constant. However, as the explicit morphology cannot be included in analytical homogenization models, it is not possible to obtain accurate prediction of microstructure properties using these methods.

In this project, we have applied a finite element modeling approach, originally developed for viscoelasticity analysis, to predict the frequency dependence of dielectric permittivity spectra in polymer nanodielectrics containing functionalized silica fillers. The dispersion state of nanofillers in the finite element model is determined from descriptor-based image characterization with statistical analyses of transmission electron micrographs, and the interfacial area surrounding the fillers is explicitly configured into the geometry. The FEA simulation is capable of going beyond the mean field approximation residing in all the homogenization methods and provides reliable predictions when interaction of the fillers and surrounding interfacial regions cannot be simply ignored. This advantage makes FEA method a suitable option dealing with the prediction of the nanocomposites in which well-dispersed fillers are expected and the distance between the fillers is not large enough for the local field to converge to the mean field.

### 2.1 Constitutive Models for Dielectric Permittivity

Relaxation behavior of the homogeneous dielectric material is commonly expressed using Debye relaxation equations, which describes the response of an ideal, noninteracting population of dipoles to the external electric field. A general expression of the Debye relaxation equation is shown as below:

\[
\varepsilon^\prime(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + i\omega \tau}
\]

where \(\Delta \varepsilon\) and \(\tau\) are the dielectric relaxation intensity and relaxation time; \(\varepsilon_\infty\) is the real permittivity at the maximum frequency. However, broadened relaxation peaks are often observed in the experiments especially for polymeric materials thanks to their less well-defined packing structures. Modification on the Debye relaxation equations is developed to account for such cases, among which the most widely used ones are Cole-Cole model, Cole-Davidson model, and Havriliak-Negami model. Empirical parameters are included into the original Debye relaxation equations to account for the broadened relaxation peak, which is often observed in the imaginary permittivity.

In the models above, empirical parameters are brought into the derivation to characterize the broadened peak mathematically. Discussions on the real physical meanings of these parameters are rarely seen in the literature. Since our modeling work is part of a Materials Genome prediction framework, we would like to avoid using these empirical parameters as best as we can. Therefore we present an alternative method hereafter based on the original Debye model, which has a clear physical meaning. In the dielectric spectroscopy of the polymer matrix, the relaxation characteristic might vary in different local regions because of the molecular weight and morphology dispersion. The broadened peak in the observed overall spectra of the polymer can be regarded as the superposition of a number of Debye relaxations. With such consideration, we adopt the following equations to describe the permittivity of dielectric polymers:

\[
\begin{align*}
\varepsilon^\prime(\omega) & = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (\omega \tau)^2} \\
\varepsilon^\prime\prime(\omega) & = \frac{\sigma}{\omega \varepsilon_0} + \frac{\Delta \varepsilon \omega \tau}{1 + (\omega \tau)^2}
\end{align*}
\]
where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary permittivity of the material. $\omega$ is the angular frequency. $\sigma$ is the dc conductivity of the material. $\Delta \varepsilon_i$ is the $i$-th dielectric relaxation strength while $\tau_i$ is the relaxation time of the $i$-th relaxation process. Through appropriate spectra analysis approaches, the overall relaxation of the polymer material can then be transformed into the summation of multiple ideal Debye relaxation processes.

Interestingly enough, these equations are in the similar form of the Prony series which are commonly used in the description of viscoelastic behavior of the polymer materials. Previous works have provided us a robust tool to solve the fitting problem for the Prony series. A simple mathematical conversion is shown hereafter to transform the Equation 2 into the form of Prony series used in the realm of viscoelasticity such that we can take advantage of the well developed fitting code.

Recall that the loss and storage moduli of the polymer in viscoelasticity are given by:

$$
E'(\omega) = E_\infty + \sum_{i=1}^{n} \frac{E_i(\omega \tau_i)^2}{1+(\omega \tau_i)^2} \\
E''(f) = \sum_{i=1}^{n} \frac{E_i \omega \tau_i}{1+(\omega \tau_i)^2} 
$$

Note that the imaginary part in Equation 2 and Equation 3 is showing the same formulation. Thus transform is only needed for the real part. Considering the limit value of the real part in Equation 2 at $\omega = 0$, one gets:

$$
\varepsilon'(\omega = 0) = \varepsilon_\infty + \sum_{i=1}^{n} \Delta \varepsilon_i 
$$

Subtract the real part of Equation 2 from Equation 4 and add the $\varepsilon'_\infty$ term, the following equation is obtained:

$$
\varepsilon'(\omega = 0) + \varepsilon_\infty - \varepsilon'(\omega) = \varepsilon_\infty + \sum_{i=1}^{n} \frac{\Delta \varepsilon_i (\omega \tau_i)^2}{1+(\omega \tau_i)^2} 
$$

The right hand side of the Equation 5 is in the same form of the real part in Equation 3. In practice, the $\varepsilon'_\infty$ and $\varepsilon'(\omega = 0)$ are approximated as the permittivity of the sample at the highest and the lowest frequency tested, respectively. With the $\varepsilon'(\omega)$ measured from the experiments, the $\Delta \varepsilon_i$ terms can be obtained through the fitting algorithm previously developed for viscoelasticity analysis. In Figure 10, the comparison between the fitted data and the experimental input is shown for epoxy matrix sample tested at room temperature.
2.2 Model Description
The COMSOL commercial software has been used to predict the dielectric spectroscopy of ceramic-filled polymer nano-dielectrics. A two-dimensional AC/DC module was set up to model the dielectric physics and explicit morphology. Geometry of the dielectric nanocomposite used in FEA simulation is obtained from microstructure characterization from TEM images. The composite microstructure used in COMSOL consists of three types of materials: polymer matrix, ceramic nanofillers, and interfacial regions between matrix and nanofillers.

Figure 11 illustrates the schematic of the FEA model for the simulation of dielectric spectroscopy. Grayscale TEM images of nanocomposite samples are first transformed into binary images following a previously developed image characterization protocol. The transformation algorithm determines grayscale threshold on pixels to distinguish between matrix and fillers in the system and outputs microstructure in
binary image with the same volume fraction (VF) as true VF from experiments. A sample binary image is shown in Figure 2 where white pixels, taking (1-VF)% of test window area, shows the polymer matrix, and black pixels of VF% of test window area represent dispersed nanofillers. The nanofillers are represented as isolated clusters of black pixels, which are equivalent to physical agglomeration of several nanoparticles. For simplicity, nanofillers are characterized as ellipses with the same area as clusters of black pixels. Major and minor axes as well as aspect ratios of ellipses are selected to surround each cluster closely. This nanofiller characterization process ensures that VF of nanofillers used in FEA is consistent with experimental value.

With the microstructure captured using the geometry directly mapped from the TEM images, the geometry feature is built in the COMSOL software package as a statistical volume element (SVE). Triangular elements are used to capture the shape of the features in the model with refined mesh in the interphase area. The AC/DC module is adopted to simulate the frequency sweep test in the dielectric spectroscopy analysis. The AC voltage is applied at the bottom surface of the sample and the top surface is grounded. The effective dielectric constant of the composites is calculated using the following equation:

$$\varepsilon(\omega) = \frac{J'_{\omega}(\omega)d}{2\pi j V'(\omega)f \varepsilon_0}$$

where $V'(f)$ is the applied voltage as a function of frequency $f$ and $J'_{\omega}(\omega)$ is the average complex AC current density along the direction perpendicular to the electrode which is measured at the grounded surface from the output of the FEA model. $d$ is the sample thickness, $j$ is the imaginary unit and $\varepsilon_0$ is the permittivity of the vacuum, which is $8.85\times10^{-12}$ F/m. The whole modeling procedure is combined in a Matlab script such that jobs are processed automatically.

Periodic boundary conditions are configured at the lateral surfaces. While the dielectric constant of the filler is taken as a constant value, the dielectric permittivity of the matrix is expressed by a complex function with respect to frequency in the form of the Debye series equations listed in the previous section and defined in the variables sections in COMSOL. At each tested frequency, the value of the real and imaginary parts of the matrix will be calculated and taken as the input properties of the matrix.

One of the core features in this modeling work is the consideration of the interphase area, which sheaths the fillers with certain thickness. To the best knowledge of us, the measurement of the interphase thickness is rarely reported in the literatures. The thickness of the interphase is estimated as 60nm in our model based on reported values from literatures. The relaxation behavior of the interphase is expressed as a superposition of Debye functions, which originates from the matrix but with additional tuning parameters:

$$\varepsilon_{\text{int}}'(\omega) = \varepsilon_{\infty} + c + M_\alpha \sum_{\tau_i > \tau_0} \frac{\Delta \varepsilon_i}{1 + (\omega S_\sigma \tau_i)^2} + M_\beta \sum_{\tau_i < \tau_0} \frac{\Delta \varepsilon_i}{1 + (\omega S_\beta \tau_i)^2}$$

$$\varepsilon_{\text{int}}''(\omega) = M_\alpha \sum_{\tau_i > \tau_0} \frac{\omega S_\sigma \tau_i \Delta \varepsilon_i}{1 + (\omega S_\sigma \tau_i)^2} + M_\beta \sum_{\tau_i < \tau_0} \frac{\omega S_\beta \tau_i \Delta \varepsilon_i}{1 + (\omega S_\beta \tau_i)^2}$$

The alpha and beta relaxations are modeled separately. Based on the experimental results, the threshold value of relaxation time, $\tau_0$, is chosen to be 1 second. Terms with $\tau_i$ greater than $\tau_0$ were modeled as alpha relaxation while those with $\tau_i$ smaller than $\tau_0$ are modeled as beta relaxation. $M_\alpha$ and $M_\beta$ account for the change in the intensity, $S_\alpha$ and $S_\beta$ characterize the shift of relaxation terms and an additional constant, $c$, describes the change in the $\varepsilon_{\text{int}}$. 
In practice we employ the following strategy while tuning the parameters in Equation 7 and Equation 8. First, the interfacial region in the FEA model is not included and the loss peak in the spectra of $\varepsilon''$ from the simulation is compared with the experimental data of the composites. Then the interfacial area is activated and the $S_\alpha$ and $S_\beta$ parameters are adjusted so that the loss peaks horizontally match the experimental data. Next the $M_\alpha$ and $M_\beta$ parameters are tuned to adjust the shape of $\varepsilon''$. Finally $\varepsilon'$ is compared and suitable adjustment is made to the additional constant $c$ which reflects the change of permittivity at $10^6$ Hz, which is caused by dipolar, ionic and electronic polarizations.

### 2.3 Results – Dielectric Permittivity

After the parameter tuning, the results of the parameters are shown in the three systems tested are shown in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_\alpha$</th>
<th>$M_\alpha$</th>
<th>$S_\beta$</th>
<th>$M_\beta$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomodal PGMA</td>
<td>4.0</td>
<td>3.0</td>
<td>0.25</td>
<td>1.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Bimodal Ferrocene</td>
<td>0.05</td>
<td>4.0</td>
<td>0.75</td>
<td>1.1</td>
<td>-0.7</td>
</tr>
<tr>
<td>Bimodal Terthiophene</td>
<td>0.02</td>
<td>0.5</td>
<td>0.75</td>
<td>1.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

As these parameters reflect the interplay between the polymer matrix and the fillers, the values are assumed to change with different combinations of the matrix and the filler but keep constant with different loadings of the fillers in a given composites. An example of the tuned process is shown in Figure 12 with 2wt% bimodal terthiophene grafted silica in epoxy is taken as the tested system.

Figure 12. Comparison between tuned spectra and experimental data in the 2wt% Bimodal Terthiophene grafted silica in epoxy. The imaginary and real permittivity spectra are shown in left and right plot, respectively.

Figure 12 indicates that the configuration of the interfacial area is essential in the modeling. A significant deviation of simulated results from experimental data can be observed if the model only composes filler and matrix without interfacial. Though the addition of surface treated silica particles does not change the location of the beta relaxation by much, the increase in the magnitude of both $\varepsilon'$ and $\varepsilon''$, is significant compared to the neat epoxy. This change, we argue, is due to the fact that the presence of nanoparticles changes the mobility of the polymer chains around them and consequently results in the alternated dielectric permittivity of the interfacial area. Therefore, the simulation accuracy can be greatly improved by including the interfacial area with shifted properties by tuning only three parameters.
Taken epoxy filled with 2wt% bimodal terthiophene silica as the example system, the real part of dielectric permittivity of the composites predicted by the homogenization models are shown in Figure 13 along with the experimental results. For the analytical models, the dielectric permittivity at each sampling frequency is calculated. Aspect ratio of the fillers is determined from the TEM images as 0.77. The dimensionless interaction parameter $K$ in Vo-Shi and Todd-Shi model are set as $10^{2.3}$ which corresponds to the interphase thickness of 60nm. Interphase properties in the 3-phase models, i.e. Vo-Shi, and Todd-Shi 3-phase model are defined based on the tuning results shown in Table 1.

As shown in Figure 13, all the 2-phase models underestimate the real permittivity of the composites, while the 3-model overestimate the real permittivity. Since the dielectric permittivity of the fillers is fairly close to that of the polymer and the volume fraction of the fillers is really small (~1%), the value predicted by the 2-phase models are almost the same as the matrix value and is quite far from what measured in the experiments. This comparison, again, renders the importance of the consideration of interphase during numerical analysis. The 3-phase models, on the other hand, gives prediction higher than the experimental value. It is explained that the overlapping of the interphase, especially when the interphase thickness is high, can show impact to the final prediction. Moreover, the orientation and the aspect ratio of the fillers in the TEM images are not exactly the same. Since these 2 factors are not considered in the 3-phase models, the models overestimates the real permittivity. Thus capturing the morphology of the composites with accuracy is important in the predictions, which, however, is not viable in the analytical models shown here.

The optimized tuning parameters for each composite system are summarized in Table 1. It can be seen that for all systems tested, $S$ is typically smaller than one and $M$ is larger than one, which indicates that the chains at the interface experienced greater mobility and enhanced polarizability compared to the bulk matrix. The parameter $c$ does not change much if there is only PGMA chain on the particle, but shows greater change as the short functional group was introduced to the nanoparticle surface. Considering that the volume fractions of these functional groups are so small (less than 0.01 % in both systems) and the dielectric constants are less than 10, it would not be sufficient to cause that much difference in dielectric constant of the molecules by their own polarizations. The difference is therefore possibly due to the change of polarizability of polymers in the interfacial region. Apparently ferrocene and terthiophene have an opposite effect on the local polarizability: ferrocene tend to depress while terthiophene tend to enhance.
But unfortunately the simulation of this phenomenon is beyond the capability of FEA. Further molecular level simulation is required to have a microscopic understanding of the phenomenon.

It should be noted that, however, the impact of the DC conductivity to the low frequency part of the spectra is neglected by assumption. As reported in previous work, the contribution to the permittivity of the DC conductivity is small compared to that of the alpha relaxation. Yet modified simulation is still needed to analyze the spectra with accuracy, based on the experimental data from quasi-static conductivity test.

2.4 Conclusion and Future Work – Dielectric Permittivity

The dielectric spectroscopy of bimodal brush functionalized epoxy nanodielectrics can be successfully simulated by FEA based on the geometry of filler distribution with interfacial area included. The relaxation behavior of the matrix was described a superposition of Debye functions, and that of the interfacial area was obtained by adjusting tuning parameters in the matrix formula. Compared to the prediction by the homogenization models reviewed, FEA models can better describe the dispersion state of the fillers as well as model the interphase region. Based on analysis of the tuning parameters, the interfacial area in our composites is likely to have an increased chain mobility and polarizability in the measured frequency range. The change of polarizations occurred at higher frequency is possibly due to the short functional groups like terthiophene and ferrocene. Future work will focus on accurately modeling the low frequency behavior and testing the model applicability to other composite systems, as well as improving the accuracy of fitting and expanding the simulation to 3-D systems.

3. Experimental Progress:

We have been continuing use the bimodal brush modification approach to carefully tailor the dispersion and dielectric characteristics of the nanoparticle/matrix interface. A new well-defined copper free grafting method was developed to eliminate any possible effect from metal residues in the matrix and effectively control and grafting density of each modal of brush. The epoxy compatible long brush poly(glycidal methacrylate) was grafted from the silica nanoparticle surface via reversible addition–fragmentation chain-transfer (RAFT) polymerization, and the short functional brush was grafted to the nanoparticle after mercaptothiazoline activation. Besides the breakdown test, an in-depth study of material dielectric properties was realized by using thermally stimulated depolarization current (TSDC) measurements and pulsed electroacoustic analysis (PEA) were used to investigate the space charge trapping behavior related to the interface. These techniques reveal the potential underlying phenomena behind the DBS enhancement.

3.1 Nanoparticle Surface Modification

3.1.1. Synthesis of Bimodal Thiophene Grafted SiO₂ Particles

3.1.1.1 Synthesis of Mercaptothiazoline activated Thiophene

2-Thiophene acetic acid (0.50 g, 3.9 mmol) was dissolved into 20ml dichloromethane along with 2-mercaptopthiazoline (0.51 g, 4.3 mmol), and 4-dimethylaminopyridine (50 mg, 0.4 mmol). The solution was cooled to 0 °C and flushed with N₂ for 20 minutes. N,N'-dicyclohexylcarbodiimide (0.80 g, 3.9 mmol) was dissolved into a minimal amount of dichloromethane and added dropwise to the thiophene acetic acid solution. The solution was allowed to warm to room temperature and stir over night. The solids were then removed via vacuum filtration and solvent was removed under reduced pressure. The crude product was then purified via column chromatography (SiO₂, CHCl₃) leaving the product as a yellow oil (0.89 g) in 95% final yield.
3.1.1.2 Thiophene grafted nanoparticles
A suspension (10 g) of 30 wt % colloidal silica in methylethyl ketone was added to a 100 ml round bottom flask with 3-ethoxydimethylsilyl-1-propanamine (90 mg, 0.56 mmol). The solution was diluted to 50ml with THF and stirred for 4 hours at 70 °C under N₂ atmosphere. Next the particles were precipitated in a large amount of hexanes and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, and upon the final wash the particles were dispersed into 30ml of THF for subsequent use. The resultant particle solution was cooled to 0 °C and flushed with N₂ before adding mercaptothiazoline activated thiophene (16.4 mg, 0.68 mmol) dropwise via syringe. The solution was then allowed to warm to room temperature and stir overnight. The thiophene coated particles were then precipitated into a large amount of hexanes and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, and upon the final wash the particles were dispersed into 30ml of THF for subsequent use.

3.1.1.3 Thiophene + CPDB coated particles
Activated CPDB was prepared as described previously. The thiophene coated particles described above were dispersed into 50ml THF along with 3-ethoxydimethylsilyl-1-propanamine. The solution was stirred at 70 °C for 4 hours. After cooling to room temperature the particles were precipitated into a large amount of hexanes and The thiophene coated particles were then precipitated into a large amount of hexanes and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, and upon the final wash the particles were dissolved into 50 ml THF. The resultant particle solution was cooled to 0°C and flushed with N₂ for 20 min before adding a solution of activated CPDB (61 mg, 0.16 mmol) in THF dropwise via syringe. The solution was then allowed to warm to room temperature and stir overnight. The thiophene + CPDB coated particles were then precipitated into a large amount of hexanes and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, and upon the final wash the particles were dried in vacuum.

3.1.1.4 PGMA + Thiophene particles
CPDB + thiophene anchored silica nanoparticles (3 g) with glycidal methacrylate (8.23 g, 57.9 mmol), AIBN (1.9 mg, 13.4 μmol), and dry THF (10ml) were added to a 50 ml Schlenk tube. The particles were dispersed into the solution via sonication for 1 minute and subsequently degassed by 4 sequential freeze pump thaw cycles. The flask was then placed into an oil bath at 60°C for 4 hours. The resultant polymer grafted particles were then precipitated into a large amount of hexanes and separated from the solution via centrifuge at 3,000 RPM for 5 minutes. The supernatant was discarded and the particles were dispersed back into THF. This washing process was repeated 3 times.

3.1.2 Synthesis of Bimodal Anthracene Grafted SiO₂ Particles
3.1.2.1 Mercaptothiazoline activated anthracene
2-(Anthracen-9-yl)acetic acid was prepared as described previously. 2-(Anthracen-9-yl)acetic acid (1.00 g, 4.2 mmol) was dissolved into 30ml dichloromethane along with 2-mercaptothiazoline (0.56 g, 4.7 mmol), and 4-dimethylaminopyridine (50 mg, 0.4 mmol). The solution was cooled to 0 °C and flushed with N₂ for 20 minutes. N,N'-dicyclohexylcarbodiimide (0.87 g, 4.2 mmol) was dissolved into a minimal

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amount of dichloromethane and added dropwise to the anthracene acetic acid solution. The solution was allowed to warm to room temperature and stir overnight. The solids were then removed via vacuum filtration and solvent was removed under reduced pressure. The crude product was then purified via column chromatography (SiO₂, 7:3, dichloromethane: hexane) leaving the product as a yellow powder (0.62 g) in 43% final yield.

3.1.2.2 Anthracene Coated Particles
A suspension (10 g) of 30 wt % colloidal silica in methylethyl ketone was added to a 100 ml round bottom flask with 3-ethoxydimethylsilyl-1-propanamine (90 mg, 0.56 mmol). The solution was diluted to 50 ml with tetrahydrofuran (THF) and stirred for 4 hours at 70°C under N₂ atmosphere. Next the particles were precipitated in a large amount of hexane and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, then the particles were dispersed into 30 ml of THF for subsequent use. The resultant particle solution was cooled to 0°C and flushed with N₂ before adding mercaptopthiazoline activated anthracene (0.23 g, 0.68 mmol) in THF dropwise via syringe. The solution was then allowed to warm to room temperature and stir overnight. The anthracene coated particles were then precipitated into a large amount of 1:1 hexane:THF solution and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, then the particles were dispersed into 30 ml of THF for subsequent use.

3.1.2.3 Anthracene + CPDB coated particles
Activated 4-cyanopentanoic acid dithiobenzoate (CPDB) was prepared as described previously [8]. The anthracene-coated particles described above were dispersed into 50 ml THF along with 3-ethoxydimethylsilyl-1-propanamine. The solution was stirred at 70°C for 4 hours. After cooling to room temperature the anthracene + amine coated particles were precipitated into a large amount of hexane and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, then the particles were dissolved into 50 ml THF. The resultant particle solution was cooled to 0°C and flushed with N₂ for 20 min before adding a solution of activated CPDB (61 mg, 0.16 mmol) in THF dropwise via syringe. The solution was then allowed to warm to room temperature and stir overnight. The anthracene + CPDB coated particles were then precipitated into a large amount of hexane and centrifuged at 3,000 RPM for 5 minutes, the supernatant was discarded, and the particles were dispersed back into THF. This was repeated 3 times, then the particles were dried in vacuum.

3.1.2.4 PGMA + anthracene particles
CPDB + anthracene anchored silica nanoparticles (1 g) with glycidal methacrylate (1.4 g, 9.8 mmol), azobisisobutyronitrile (AIBN) (0.3 mg, 2.0 μmol), and dry THF (3 ml) were added to a 25 ml Schlenk tube. The particles were dispersed into the solution via sonication for 1 minute and subsequently degassed by 4 sequential freeze pump thaw cycles. The flask was then placed into an oil bath at 60 °C for 4 hours. The resultant polymer grafted particles were then isolated by centrifugation at 20,000 RPM for 1 hour. The supernatant was discarded and the particles were dispersed into THF. This washing process was repeated 3 times.
3.2 Sample Characterization and Discussion

Nanoparticles as modified in Table 2 in solution were mixed with Huntsman Araldite GY 2600; a bisphenol-A based epoxy resin using a Hauschild high shear mixer. Solvent was then evaporated in vacuum. Silica loading was measured with thermo gravimetric analysis (TGA), whereupon the composite resin was diluted to achieve the desired loading and mixed with aliphatic amine based Huntsman Aradur 956-2 using the same high shear mixer and then cast into samples. Recessed samples for breakdown tests and flat samples for TSDC and PEA were prepared as described in the literature.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Short Brush/graft density</th>
<th>PGMA Mw/graft density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloidal Silica</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Monomodal PGMA</td>
<td>NA</td>
<td>17k/0.15 nm⁻²</td>
</tr>
<tr>
<td>Bimodal Anthracene</td>
<td>Anthracene /0.28 nm⁻²</td>
<td>Short Chains/0.11 nm⁻²</td>
</tr>
<tr>
<td>Bimodal Monothiophene</td>
<td>Monothiophene /0.44 nm⁻²</td>
<td>10.7k/0.14 nm⁻²</td>
</tr>
</tbody>
</table>

3.2.1 AC Breakdown Test

The AC breakdown strength was measured for all the composite samples. The dielectric breakdown strength (DBS) was evaluated from recessed samples. Breakdown results were fitted with a 3-parameter Weibull distribution, whose cumulative distribution function is given by

\[ F(x) = 1 - \exp\left\{ -\left( \frac{x - \xi}{\alpha} \right)^\beta \right\} \]

where \( F(x) \) gives the probability of breakdown at certain electric field strength \( x \) (V/µm). The scale parameter \( \alpha \) is related to the 63.2% probability of breakdown at field strength \( \alpha \), and the shape parameter

---

$\beta$ describes the shape of the distribution; the higher the value of $\beta$, the narrower the spread of individual breakdown strength results. The threshold value $t$ is used to better fit the data.

The distribution of breakdown strength values for the tested composites are shown below in Fig. 15. Of note are the progressive improvements seen in the DBS, (Table 3). Filler modified with a monomodal brush for matrix compatibility shows a small improvement; while anthracene and PGMA bimodally modified fillers show greater improvements up to 27% over the neat polymer.

![Figure 15. Weibull fit of breakdown data](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shape</th>
<th>Scale (kV/mm)</th>
<th>95% confidence interval (kV/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>4.3</td>
<td>198</td>
<td>21</td>
</tr>
<tr>
<td>Colloidal Silica</td>
<td>4.4</td>
<td>192</td>
<td>22</td>
</tr>
<tr>
<td>Monomodal PGMA</td>
<td>3.7</td>
<td>228</td>
<td>25</td>
</tr>
<tr>
<td>Bimodal Monothiophene</td>
<td>5.9</td>
<td>216</td>
<td>14</td>
</tr>
<tr>
<td>Bimodal Anthracene</td>
<td>4.4</td>
<td>246</td>
<td>20</td>
</tr>
</tbody>
</table>

3.2.2 Dielectric Spectroscopy Test

Dielectric spectroscopy was used to study the dielectric constant and loss as a function of frequency from $10^{-5}$ Hz to $10^6$ Hz, shown in Figure 16. The introduction of the nanoparticle has slightly increase the dielectric constant by ~5%, and different short molecules show varied effects on the dielectric constant, which is probably caused by the resulted change of the polarizability of polymer chains at the interface. The peak showed in the imaginary permittivity around $10^4$ is due to the crankshaft motion of the side chain of epoxy, and the low frequency increasing slope is caused by the backbone chain motion. It can be seen that the presence of nanoparticles have generally enhanced the mobility of the polymer chain at the interface and thus resulted in a larger loss at low frequency. This effect is more significant for samples filled with bimodal modified particles because of the larger surface area in those samples from good dispersion. This was confirmed by the TEM images shown in Figure 17.
3.2.3 Pulsed Electro-acoustic (PEA) Test

The PEA test was used an aluminum bottom electrode and a carbon black loaded semi-conductive polymer upper. Transformer grade silicone fluid was used between the sample and the electrode to reduce the acoustic attenuation. The probe pulse used had a width of 10 ns, a repetition frequency of 140 Hz and amplitude of 300 V. A dc voltage of -20 kV (electric field = 60 kV/mm) was applied to samples via the
top electrode for 1 hour at room temperature and the depolarization charge profile was measured immediately after voltage removal for 1 hour.

![Figure 18. Space charge measured at various times during polarization (left plot) and depolarization (right plot). The anode is the bottom electrode and the cathode is the top electrode.](image_url)

The space charge profile of neat epoxy during polarization is shown in Figure 18. The displacement of the peak front indicates the presence of injected charges of the same polarity as the electrode. Most injected charge was trapped in the vicinity of the electrode without traveling into the bulk, in agreement with previous results\(^4\). Little difference was observed for each sample in the space charge profile under field due to the strong influence of the image charges and limited spatial resolution of the test system.

The depolarization space charge profile confirmed that the injected charges were trapped near the electrode (Figure 5). The signal from cathode is less accurate due to the attenuation and dispersion of the acoustic wave, so we concentrate our analysis decay on the homocharge peak close to the anode, where the acoustic signal is collected. The space charge decay profiles are plotted in Figure 6. The space charge density was obtained by integrating the homocharge peak next to the anode. We applied the detrapping model proposed by Dissado\(^6\), wherein he assumed a square distribution of traps and found that the charge density is logarithmically proportional to the decay rate. Dissado's equations are shown below.

\[
\begin{align*}
\rho(t) &= \rho(0), \quad t < [v \exp(-\Delta_{\text{max}}/kT)]^{-1} \quad (1) \\
\rho(t) &\approx [\rho(0)kT/(\Delta_{\text{max}}-\Delta_{\text{min}})][(u - \ln(t))] \\
[v \exp(-\Delta_{\text{min}}/kT)]^{-1} &< t < [v \exp(-\Delta_{\text{max}}/kT)]^{-1} \quad (2) \\
\rho(t) &= 0, \quad t > [v \exp(-\Delta_{\text{max}}/kT)]^{-1} \quad (3)
\end{align*}
\]

Here \(v\) is the attempt to escape frequency; \(\rho(t)\) is the space charge density at time \(t\); \(\Delta_{\text{max}}\) and \(\Delta_{\text{min}}\) represents the maximum and minimum trap depth respectively; and \(a\) is the time independent factor. A plateau can be clearly seen for monomodal PGMA and bimodal anthracene samples, implying the existence of deep traps. Therefore we used two square distributions of traps to better capture the decay (shown as two lines in Figure 19). The minimum trap depth was taken as 0.79 eV for all samples, calculated from the minimum observable relaxation time of 5 seconds. The maximum trap depths were calculated from the longest relaxation times taken from the intercept value on the time axis for each fitted line respectively. The occupation percent for each distribution is calculated from the total charge and decay associated with each distribution. The results are summarized in Table 4. The introduction of silica

nanoparticles increases the maximum trap depth for holes by 0.10 eV while the anthracene modified silica nanoparticles were increased the depth by 0.22 eV.

Figure 19. The decay space charge density of various. Dotted lines are fitted to the slopes of the decay curves, one for each trap distribution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Neat epoxy</th>
<th>Monomodal PGMA</th>
<th>Bimodal Anthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trap Depth (eV)</td>
<td>min</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>0.92</td>
<td>1.04</td>
</tr>
<tr>
<td>Occupation%</td>
<td></td>
<td>63%</td>
<td>37%</td>
</tr>
</tbody>
</table>

3.2.4 Thermally Stimulated Depolarization Current (TSDC)

TSDC tests were carried out on flat samples identical to those used for PEA tests. The samples were heated to 120°C and polarized at 15 kV/mm for 20 minutes. They were then quenched with liquid nitrogen. Surface charges were removed with a 5 minute short-circuit, and the sample was then shorted across a sensitive current meter while the temperature was ramped at 0.5°C/minute.

TSDC data was collected from unfilled epoxy samples and from samples filled with silica nanoparticles bimodally modified with PGMA and anthracene. The data, seen in Figure 20, demonstrates an additional peak at low temperatures, as well as a shift in the location of the intrinsic neat epoxy low temperature peak. The appearance of a new peak is attributed to the introduction of a uniform population of traps related to the anthracene modified filler. The shift to higher temperatures of the low temperature intrinsic peak is likewise attributed to enhanced trapping of charge due to the filler, which slows the decay of charge, as seen in the PEA results. The values of the activation energy for these peaks were calculated per the Bucci-Fieschi theory, and can be seen in Table 5.

The DBS results demonstrate the efficacy of a ligand-engineered filler with compatibilizing and functional molecules in the brush. Additionally, the importance of the nanofiller itself is critical, as the epoxy with free anthracene included displays a significant decrease in DBS compared to the neat epoxy, while anthracene grafted to the nanofiller surface significantly improved DBS. We attribute this to the traps associated with the anthracene. When evenly distributed as free molecules, they may increase hopping conduction and thus reduce the DBS. Conversely, when they are localized at isolated particle surfaces, their trapping behavior reduces the mobility of space charge, increasing the DBS. This theory is supported by the trap population analysis obtained from space charge decay results in the PEA tests. Detectable increases in deeper traps are attributed to the nanoparticle filler, and significantly enhanced by
surface modification of the filler with anthracene. TSDC results corroborate this theory, revealing increases in trap depth similar to those seen in the PEA, as well as revealing a new type of trap in the composite.

![Figure 20](image)

Figure 20. Thermally stimulated depolarization current data from a neat epoxy sample and a bimodal anthracene sample polarized at 15 kV/mm and an unpolarized neat epoxy sample. Peaks are labeled corresponding to Table IV

<table>
<thead>
<tr>
<th>Trap Depth of Peak (eV)</th>
<th>Neat epoxy</th>
<th>Bimodal Anthracene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NA</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>0.35</td>
<td>0.43</td>
</tr>
<tr>
<td>3</td>
<td>0.51</td>
<td>0.68</td>
</tr>
</tbody>
</table>

**3.2.5 Polypropylene/SiO$_2$ Nanocomposite System**

This ongoing work is not funded through this ONR project but is relevant for modeling purpose. We present here to show the efficacy of bimodal surface ligand engineering in other polymer nanocomposites for high performance dielectric materials.

Silica nanoparticles were grafted with poly(stearyl methacrylate) (PSMA) to improve the dispersion in polypropylene (PP). The long side chain of stearyl methacrylate is polyolefine like and would help the entanglement with the polypropylene matrix. The polymer is grafted from the nanoparticle by RAFT, and the general scheme is shown in Figure 21.

The nanocomposites shows increased dielectric constant and loss over the frequency from 0.01 Hz to $10^6$ Hz, as shown in Figure 22.
Figure 21. The synthesis route for PSMA grafted silica nanoparticle.

Figure 22. The dielectric spectroscopy of PP nanocomposites filled with PSMA grafted silica nanoparticles of 0.14/nm² grating density.

A bimodal modification was achieved by grating anthracene molecules to the PSMA grafted silica nanoparticles. The anthracene molecules contribute to electronic charge trapping and improve the breakdown strength up to 28% at 2wt% loading of silica. The results were shown in Figure 23.
3.3 Conclusions and Future Work - Experimental

Surface modification of filler particles can significantly increase DBS, and these increases are correlated with increases in the number, depth, and occupancy of deeper traps. These traps are associated with the filler surface ligands, but the ligand molecules by themselves are not sufficient to generate the improvements in DBS. Thus, both the surface chemistry of the filler, and the inhomogeneous physical distribution of traps are central to the properties seen in these composites.

Apart from the SiO$_2$/epoxy nanocomposites system, we will explore our bimodal surface ligand engineering on other nanocomposites systems including silicone/titania, zirconia system grafted with various small functional molecules. A systematic in-depth investigation on the material dielectric properties will be continued to study the effect of fillers: SiO$_2$, TiO$_2$, ZrO$_2$, etc. and the effect of small molecules with different HOMO and LUMO levels so as to validate the hypothesis from the first principle calculation.

Publication

“Dielectric Spectroscopy Analysis on Polymer Nanodielectrics Using Homogenization models and FEA Simulation”, by Yang Li, He Zhao, Ke Wu, Yanhui Huang, Timothy Krentz, Hongyi Xu, Wei Chen, Curt Breneman, Linda Schadler, and Cate Brinson (manuscript in preparation) will cover recent development of the FEA model developed. This model is the first of its kind to take into account the dispersion of a secondary phase and to use a Prony series approach to model the relaxation times in the composite. It is potentially a very powerful tool for designing nanocomposites with controlled dielectric spectra.

Invited Talks

LC Brinson and W Chen, Northwestern-Shanghai Jiaotong University, Workshop on Engineering Mechanics, December 14, 2013, Materials Genome Initiative for Global Competitiveness
LC Brinson, University of Dortmund, Localized Polymer Response and a Materials Genome Approach for Nanocomposite Propery Prediction, 30 January 2014.
LC Brinson, University of Toronto, Local Polymer Behavior: Surfaces, Confinement, Composites, 17 January 2014.
2014 IEEE Conference on Electrical Insulation and Dielectric Phenomena, Des Moines, Iowa
“Prediction of Interface Dielectric Relaxations in Bimodal Brush Functionalized Epoxy Nanodielectrics by Finite Element Analysis Method” Yanhui Huang, Timothy M. Krentz, J. Keith Nelson, Linda S. Schadler, Yang Li, He Zhao, L. Catherine Brinson, Michael Bell, Brian Benicewicz, Ke Wu and Curt M. Breneman

2014 IEEE Conference on Electrical Insulation and Dielectric Phenomena, Des Moines, Iowa “Enhanced Charge Trapping in Bimodal Brush Functionalized Silica-Epoxy Nanocomposite Dielectrics” Timothy M. Krentz, Yanhui Huang, J. Keith Nelson, and Linda S. Schadler, Michael Bell and Brian Benicewicz, Su Zhao and Henrik Hillborg

Curt M Breneman, Ke Wu, Linda Schadler, Cate Brinson, Decrypting the materials genome with materials informatics: One length-scale at a time, Frontiers in Computational Methods for Polymeric Materials, PMSE: Division of Polymeric Materials Science and Engineering, ACS, August 10, 2014, San Francisco, CA

Curt M Breneman, Ke Wu, Linda Schadler, Cate Brinson, Yang Li, Richard Zhao, Yanhui Huang, From QSAR To MQSPR and beyond: Using materials informatics to predict the mechanical and dielectric properties of polymers and nanocomposites using a combination of heuristic and physics-based methods, Ameri-QSAR, COMP: Division of Computers in Chemistry, ACS, August 10, 2014, San Francisco, CA

Curt M Breneman, Ke Wu, Lisa Morkowchuk, Linda Schadler, Cate Brinson, Yang Li, Michael Krein, Hybrid materials informatics (MQSPR) and simulation methods for predicting the thermomechanical and dielectric properties of polymers and nanocomposites, Chemical Mechanisms in Advanced Materials, COMP: Division of Computers in Chemistry, ACS, September 9, 2013, Indianapolis, Indiana


Ke Wu and Curt Breneman, Combining Heuristic and Physics-Based Methods for Predicting Nanocomposite Properties, Information Science for Materials Discovery and Design, February 5, Santa Fe, New Mexico

Curt Breneman, Combinatorial data analytics and MGI, White House OSTP Meeting Combinatorial Workshop, May 5-6, 2014, San Francisco, CA

Curt Breneman, From QSAR to MQSPR and Beyond: Predictive Materials Informatics Using a Blend of Heuristic and Physics-Based Methods, August 31-September 4, 2014, St. Petersburg, Russia