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Polymer nanodielectrics—Short history and future perspective EP

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ABSTRACT

This article provides a perspective on the development of polymer nanodielectrics for electrical insulation applications. It includes a short history of the development of the field, barriers to implementation, a chemical toolbox available for optimizing properties, some examples of potential commercial development, and the latest advances. It offers opinions on critical research needed to fully develop the models needed to predict the behavior and to develop design tools. Key findings include the need for quantification of nanofiller dispersion, investment in long term aging data research, better scale-up methods, a data resource that brings the broad data together in a format that enables faster scientific discovery, and a commercial entity willing to take the risk in implementing these promising materials.

I. INTRODUCTION

Nanodielectrics have immense potential to improve the performance of applications ranging from high-voltage electrical transmission components to small-scale electronics to sensors and more. Nanodielectrics are a 21st century phenomena. They are part of the larger field of composites consisting of a matrix (usually a polymer, but not necessarily so) and a filler or fillers with at least one dimension less than 100 nm and typically less than 30 nm. A common example would be a polymer in which inorganic oxide nanoparticles are incorporated to form an electrically insulating material with enhanced properties. As shown later, however, there are a myriad of combinations being explored, combined with chemical modification of the particles, and different processing methods to control the ultimate morphology. This is a wide open space for materials development.

While traditional composites typically require a trade-off in properties (particularly the electric strength), nanodielectrics often exhibit unique combinations of properties important for dielectric applications and could have a significant commercial impact. There has been some exciting commercial investment in the development of nanocomposites for applications such as capacitors (Sec. V C) and silica filled epoxy for motor/generator insulation.[1] Their potential, however, has not been fully realized due, in part, to the risk of introducing a new material to applications that require years or

decades of service, as well as limited fundamental understanding of the mechanisms controlling performance and how to optimize properties.

In the following paragraphs, a short history is provided, and then the barriers to implementation are presented followed by the toolbox available for nanodielectric materials' design and optimization. The perspective then turns to the most relevant properties from a commercial perspective via three example applications and the path forward for these materials to meet their potential for improving the efficiency of electrical generation and transmission, and the functionality of capacitors. This is followed by some of the most interesting new ideas in nanodielectrics research.

II. HISTORY AND ORIGINS OF NANODIELECTRICS

Electrical insulation is widely regarded as a "mature science" because materials such as polyolefins, epoxy, and mineral oil have endured substantially unchanged for many decades. Even a 10% improvement in a key property is regarded as significant for these traditional materials. In 1994, however, the late Professor T. John Lewis published a paper on "nanodielectrics."[2] Lewis's paper was a theoretical contribution that predicted a new major field of insulation in which properties are dominated by the large volume of filler/matrix interfacial region characterized by a diffuse double layer similar to that known to exist in dielectric fluids.
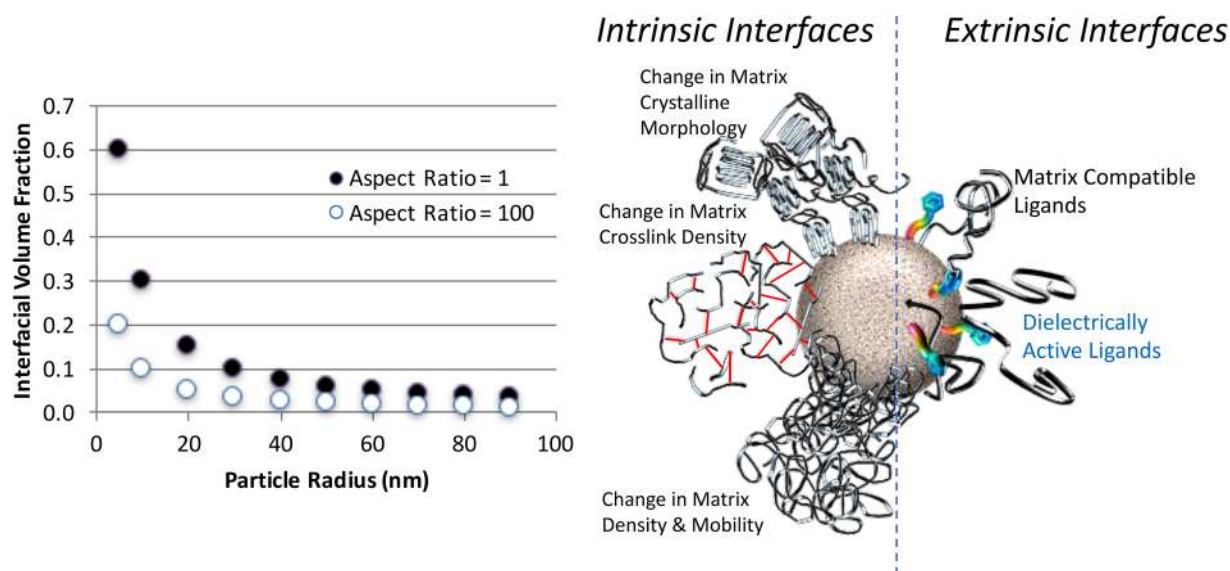
FIG. 1. A plot of the interfacial volume as a function of particle radius for spherical and elongated particles, and a schematic of the intrinsic and extrinsic interface.

Although there were some indications in the patent[3] and other[4] literature that his prediction was correct and small particulates could have benefits, it was not until the early 2000s that several groups started reporting interesting properties as a result of nanoscale particle size.[5–7] These were relatively crude, early attempts to disperse nanofillers in polymers with limited success, but still demonstrated significant changes in dielectric properties, most notably dielectric breakdown strength (DBS) and voltage endurance.

It quickly became clear that Lewis's insight was correct. Not only was the small size of the particles important (as small defects and as distributed traps), but the physics and chemistry of the interfacial region were critical to the ultimate properties[8] (Fig. 1). This interfacial region can be categorized into two regions: intrinsic interfacial regions, which are the result of changes in the matrix structure,[9–11] mobility,[12,13] or cross-link density[14] and perhaps exhibit the double layer suggested by Lewis; and extrinsic interfacial regions, which are the result of ligands on the surface of the fillers, particularly resulting from functionalization. The extrinsic interfacial region can be extensive and tailored as charge trapping regions, or regions of altered conductivity or permittivity.[15–17] In nanodielectrics, this interfacial region is a substantial volume fraction of the material even at low particle loadings ultimately requiring that the design of the nanodielectrics consider not only the filler and matrix properties but also the properties of the interfacial region.

Indeed, a new field has opened up. Several reviews and books,[18–20] special sessions at dielectric conferences, and dedicated issues of journal publications, the most recent of which is an excellent special issue from 2020,[21–25] are a testament to Lewis's foresight.

Figure 2 shows results from many papers that demonstrate an increase in dielectric breakdown strength (DBS) over a broad set of

systems. Clearly there is something fundamental about the size of the fillers that is leading to enhanced properties. Note that the negative values are likely due to poor processing and filler dispersion (see Sec. III). Figure 3 illustrates one of the first reports of the 1 to 2 orders of magnitude improvement in voltage endurance (life at a given electric field) observed. Note that endurance is not widely reported in the literature but captured the interest of the industry. Some of these improvements demonstrated in the literature are sufficiently dramatic that nanodielectrics are now being used in industrial applications, and some of the emphasis is shifting from the research laboratory to addressing the problems anticipated in the scale-up of the methodology.[1,26]

III. BARRIERS TO IMPLEMENTATION

In our experience working with companies, the most critical barrier to commercial implementation has been achieving the level of filler dispersion required for the composites to exhibit improvements in properties in samples processed on an industrial scale and the lack of data on the long term performance of these materials due to aging. Additional barriers include: a consistent set of data upon which to build models and design approaches, models that capture the full multiscale complexity of breakdown and aging, a materials design approach based on high quality data and multiscale models that can drive the choice of filler type, filler functionalization, matrix, and processing conditions to achieve the short and long term properties required in the field, and cost.

Figure 4 shows the DBS vs filler dispersion (described by the nearest cluster distance) for a few systems indicating the strong role of dispersion on DBS as well as the dependence on constituent properties. As the fillers agglomerate, the most notable impact is
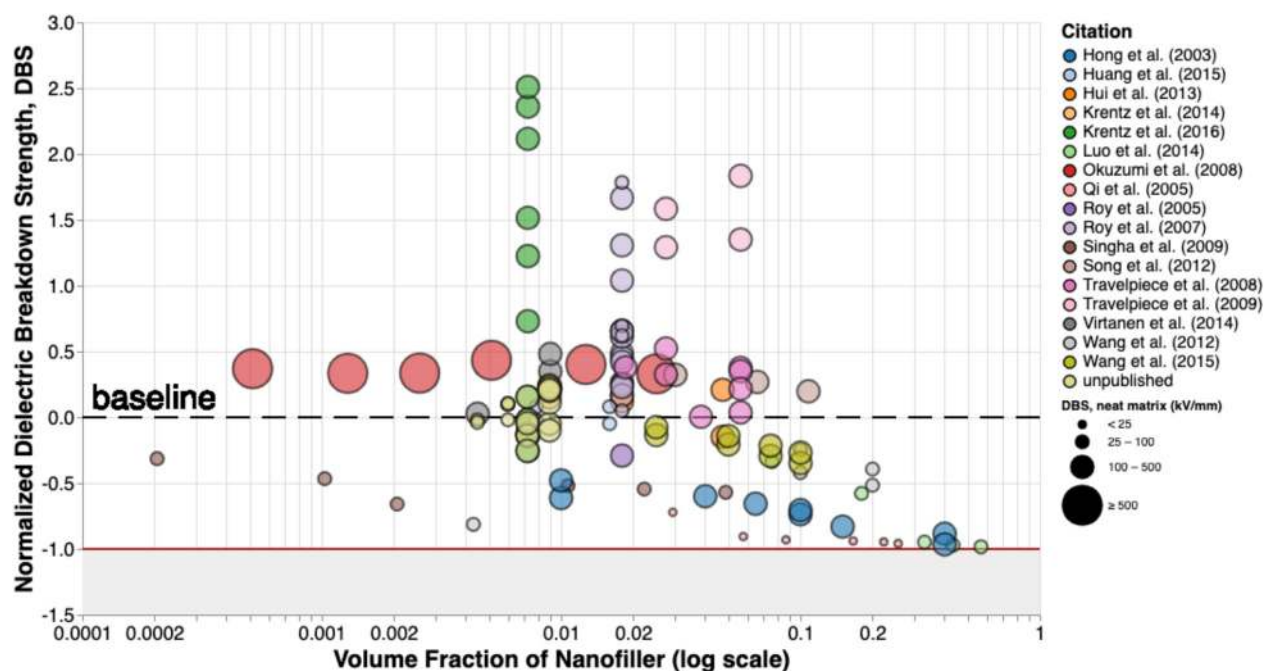
FIG. 2. Data gathered from the NanoMine Data Resource (MaterialsMine.org). Normalized dielectric breakdown strength vs volume fraction showing that in many materials a significant increase is observed.[15,27–42] The size of the dot corresponds to the dielectric breakdown strength of the neat matrix, and for cases where the same volume fraction is leading to different DBS, typically the filler surface has been chemically modified to either alter dispersion or impact carrier transport.

that the interfacial area/volume decreases and the distance between particles increases for a given volume fraction. Ultimately, agglomerated systems act in a similar fashion to micrometer scale fillers decreasing DBS. The permittivity and loss are also impacted by dispersion and the properties of the interface dictate whether the permittivity increases or decreases with improved dispersion.[44,45]

Thus, *one key barrier to commercial application* is that the published work rarely quantifies the dispersion, making it difficult

to compare across laboratories and determine the commercial processing outcomes required. In some cases, there are a few images of the dispersion, suggesting good or poor dispersion, and then the properties are reported, but rarely is there a correlation done
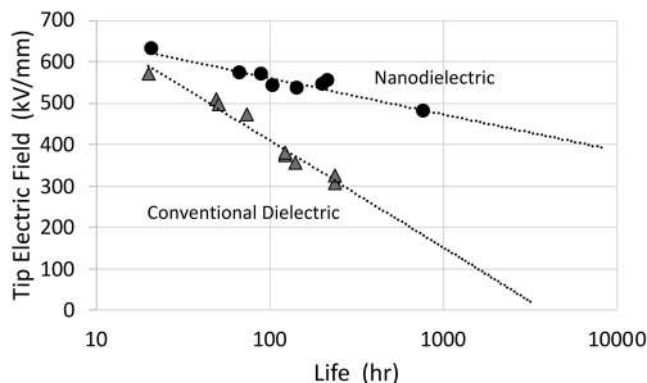

FIG. 3. Divergent-field voltage endurance characteristics for TiO_2-epoxy composites. Upper: nanodielectric; Lower: conventional.[43]
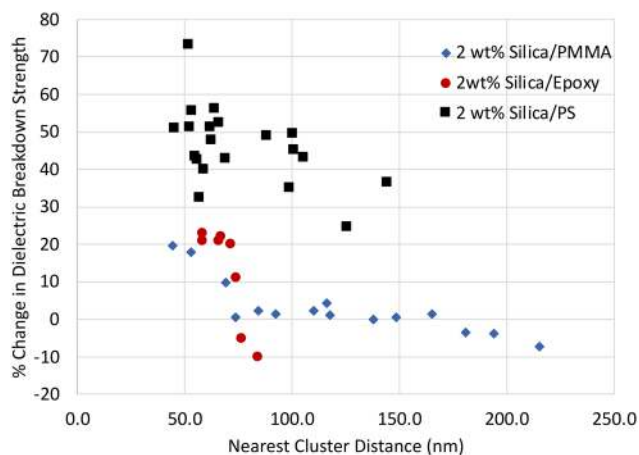

FIG. 4. The impact of particulate dispersion of the dielectric breakdown strength. The smaller the nearest cluster distance, for a given loading, the better the dispersion.

between quantified dispersion and properties. To move this field forward, and allow the design of materials, the data presented in the literature needs to be accompanied by data quantifying the dispersion, and data needs to be in a shared resource such that the community can learn, quantitatively, about the impacts of different fillers and filler surface chemistries on behavior.

There are many ways to quantify dispersion. Scattering can provide a quantitative measure of dispersion in a large sample but does not always capture the critical subtleties.[46] From image analysis of transmission electron microscopy or atomic force microscope images, the cluster size, intercluster distance, interfacial area, skewness of the distribution, and more can all be determined in a small volume, but it is unclear if a representative volume element has been sampled.[47–49] Two point correlation functions can also be determined from those images and can quickly be used to build equivalent structures for use in modeling.[50–52] A free space parameter has also been used. It is a measure of the space between particles or particle clusters.[53] It would be beneficial if the community agreed on a method to quantify dispersion, and the reviewing community enforced a more robust approach to reporting on dispersion. This would support the development of a cross laboratory set of data that could be used to validate models and develop a design-based approach.

Another significant barrier to the use of these materials is a lack of data on the aging behavior. The industry (with good reason) is reluctant to use new materials without understanding fully their degradation behavior over time. This includes the impact of moisture, the damage to the materials over time, the changes in mechanical integrity, and more. The solution to this requires pilot scale-up studies with real part geometries tested over long times.

The work that has been published on aging shows that the introduction of well-dispersed nanoparticles, while showing substantial advantages, also provides an extensive pathway for moisture through the bulk material. The migration of moisture is thus of particular concern when the material is used as a dielectric since it represents an ionic contaminant. Many insulating materials need to be utilized in high-humidity environments and electrochemical treeing is a known failure mechanism, particularly in high-voltage cables[54] under the combined influence of humidity and electric field. Studies of nanodielectrics make it very clear that the migration of moisture is, indeed, enhanced,[55] although there are indications that the benefits of the technology outweigh the negative effects of the water ingress,[33] and there may be ways to mitigate water ingress through particle functionalization.[56]

Scale-up processing is also a barrier. Many of the most exciting properties have been observed in systems with highly tailored molecules on the surface of the fillers. At the moment, this type of surface modification has not become a standard technology for use in large-scale operations. Furthermore, it is inherently more difficult to achieve good dispersion on large-scale systems than is possible in a small-scale laboratory environment where parameters can be closely controlled. This is not just a challenge for nanodielectrics, but for particle filled polymers in general, where processing is more an art than a science. Finally, nanofillers tend to significantly increase polymer viscosity[57] making infiltration and molding in complex geometries challenging.

The lack of data at several scales of samples size, lack of aging data, and poor characterization of dispersion mean that there is not enough high quality published data. Without enough data on properties and aging as a function of dispersion and filler functionalization, the multiscale models that include the interface cannot be validated, limiting the potential for a design-based approach to materials development. *These are three critical barriers.* The lack of high- quality data could be addressed through some specifications on testing approaches and required reporting of processing and dispersion information. The models are beginning to improve,[58,59] and there are attempts to bring them into a design approach.[60] A more coordinated and well supported effort would lead to faster development and commercial insertion.

Finally, cost could be a significant barrier. Nanodielectric formulation is clearly more costly than the base polymer. However, empirical studies have shown that, for many applications, only a few percent loading is needed to bring about changes. Consequently, this route could be cost effective if the processing can be managed.

Thus, for the industry to successfully translate what has been learned in research laboratories to application, a sustained effort on understanding the role of dispersion on properties, the impact of aging (and the ability of interface functionalization to mitigate) is critical as well as an investment in new mixing approaches that lead to controlled dispersion even at scale. These will likely have to be processing lines that go from surface modification straight into mixing in order to prevent the need for drying of these high surface area materials. We then need enough data and multiscale models to develop a robust design approach, the type that leads to fiber based composites ultimately being used in high-end applications. Ultimately, cost will be an important consideration, but as the use of materials increases, costs often decrease and the volume fraction of fillers required to achieve significant changes in properties is small.

IV. OPPORTUNITIES—THE TOOLBOX AND APPROACHES TO INTERFACE DESIGN

In recent years, the community has done significant work understanding how to optimize the properties of nanodielectrics using nanoparticle surface "ligand engineering" and modification of the matrix polymers.[61–63] One key focus is using ligands that compatibilize the particle with the matrix and lead to good (or controlled) dispersion. For particles smaller than the radius of gyration of the matrix chains, and a surface that is enthalpically compatible with the matrix (a Flory–Huggins chi parameter of zero[64]), the propensity to disperse increases significantly.[65] As the particles become larger than the radius of gyration, the reduced entropy of the matrix chains, excluded volume, and van der Waals core–core attractions of the particles result in a higher propensity to aggregate.[63]

Small ligands (e.g., silane or phosphonate coupling agents) can be used to improve the enthalpic compatibility, but that limits the ability to also place ligands on the surface that enhance the dielectric properties. There was some beautiful work[17] using phosphonate linkages to attach molecules of varying electronegativity and demonstrating a correlation between electronegative polarity and increased DBS as well as decreased leakage current. The results
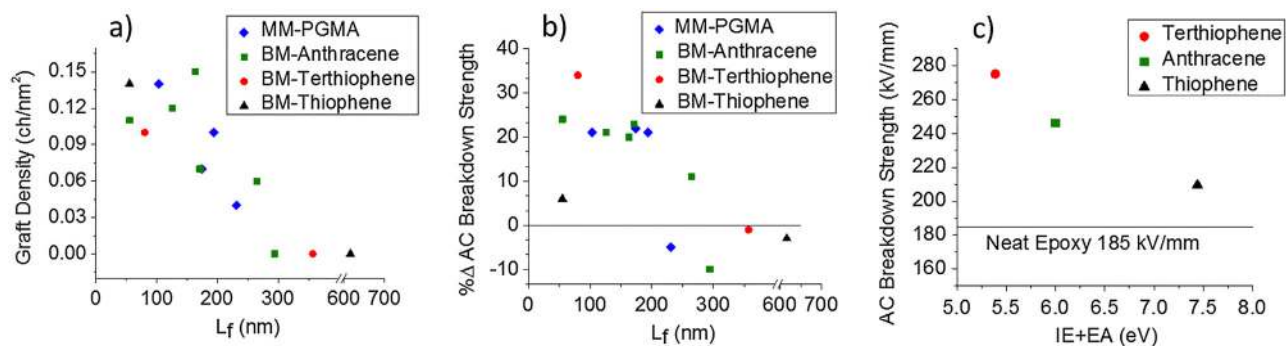
FIG. 5. (a) The impact of epoxy compatible ligand graft density on the dispersion, as measured by the free space parameter (lower L_f is better dispersion), (b) the subsequent impact of the free space parameter on breakdown strength, and (c) the impact of the molecule ionization energy (E) plus electron affinity (EA) on the maximum breakdown strength for well-dispersed samples. Reprinted with permission from Bell *et al.*, J. Colloid Interface Sci. **495**, 130 (2017). Copyright 2017 ACS Publications.

were challenged, however, because the ligands used did not lead to individual particle dispersion and the impact of dispersion was unclear. This, however, shows the promise of tailoring the functional group electronic properties to optimize the dielectric response.

A toolbox of techniques for grafting longer ligands (polymers) either "to" or "from" the particle surface has allowed both enhanced dispersion and molecular tailoring. A "monomodal" (MM) population of grafted chains requires a specific window of grafted chain density and molecular weights, and again, the chemistry is chosen to increase compatibility, not dielectric properties.[66] A "bimodal" (BM) population of ligands allows a low graft density of long chains with the same chemistry as the matrix to control dispersion combined with a high graft density of short ligands that provide enhanced dielectric properties. The value of this approach has been demonstrated in a few systems,[41,67] most notably the increase in DBS and voltage endurance as a function of the graft density. Figure 5(a) shows the impact of long epoxy compatible chain graft density on the free space parameter, L_f (a measure of dispersion[41]). Figure 5(b) shows the impact of L_f on breakdown strength suggesting that better dispersion leads to higher breakdown strength. Figures 5(b) and 5(c) also demonstrate that the impact of the dispersion is system dependent and that the higher the sum of the ionization energy (E) plus the electron affinity (EA) of the high graft density short molecule, the larger the impact of dispersion and the higher the breakdown strength.

Once the ligand engineering approach is adopted, the question becomes which ligands to use. While Siddabattuni *et al.*[17] demonstrated the value of controlled modification of a given molecular properties (such as electronegative polarity), the concept of using large datasets and machine learning to direct the next materials system is of high value. There are efforts to do this for spherical nanofilled polymers with tailored interfaces, but it is nascent and limited.[60] In pure polymer systems, progress has been significant, and notable work by Mannodi and Ramprasad has resulted in new classes of polymers,[68] most recently, metallic additions to polymers such as Sn and Cd.[69] This approach should be taken across the board.

An even newer approach is to use combinations of particles and high aspect ratio fillers to prevent agglomeration of the high aspect ratio fillers, such as multi-walled nanotubes (MWNTs), and to take advantage of extra high permittivity materials. An excellent example is the work by Liu *et al.*[70] where the combination of calcium copper titanate particles covalently bonded to MWNT via a ligand linkage results in a permittivity of over 2000 and a loss tangent of less than 0.2. While this is not directly relevant for insulators, it is a good example of how combining nanomaterials can lead to tailored properties.

An alternative to combining materials via covalent linkage is the formation of core/shell particle structures with highly conductive materials in the core and an insulating shell.[71] The conductive filler increases the permittivity, while the insulating shell prevents the percolation of the conductive cores. Others have found ways to create 2D layers of materials either through formal planar layering or through organization of fillers into sheets or strings that can also lead to interesting properties.[18,72,73] The naturally occurring 2D materials have also been explored with significant success when they can be well dispersed,[74,75] but there has been less emphasis on them.

To fully realize the potential of nanodielectrics, large-scale processing of fillers with ligands of controlled chemistry, molecular weight, and graft density will need to be available.

V. A FEW EXAMPLES OF POTENTIAL INDUSTRIAL APPLICATION

Industrial application of nanodielectrics will require that the multiscale models and design approaches have the flexibility to be application specific. For example, of the three fundamental attributes of insulating materials [electric strength, relative permittivity, and dielectric loss (tan δ)], the electric strength is typically the most important (and a 30% enhancement over the base polymer is typical, substantial, and extremely useful). However, high values of relative permittivity, which would be desirable for a capacitor, might be a huge disadvantage for a cable dielectric or for stress control in mixed material systems. Similarly, a low loss, valuable for cable insulation, is not always necessary for field grading materials. Thus, not only do we need to control dispersion, understand the contributions of the interface, measure aging, and scale-up

processing, we need to have the design tools that will allow tailoring of the constituent properties to meet the requirements of the bulk material for a specific application.

In addition to the three properties cited above, several other characteristics can be pivotal in specific situations. Examples include mechanical properties, thermal conductivity, erosion resistance, and treeing propagation. Building these properties into a design optimization will likely only occur at the macro-scale design level.

A comprehensive review of nanodielectric attributes can be found elsewhere.[19] But, for the purposes of this paper, we have chosen three examples to illustrate how the unique properties of nanodielectrics may be used in the industrial context either by capitalizing on multifunctionality or by utilizing a substantially enhanced property such as voltage endurance or erosion resistance. However, the elevated electric strength, in particular, makes nanocomposites attractive for a wide range of other insulation applications. In the high-voltage power arena, that would include cables, outdoor insulators, bushings, and other support structures.

A. Applications in generators and motors

Changing the insulation type is a big step for the original equipment manufacturers (OEM) since the implications of failure are immense, and the current epoxy-mica formulation has served the industry well for several decades. However, one of the largest benefits of nanodielectrics is the enhancement of voltage endurance, which is also the least reported. In addition, the observed enhancement in the short-term AC breakdown strength of about 30% offers the possibility of increasing the working electric stress and/or reducing the groundwall dimensions. This not only permits a more compact machine design but has thermal implications since the electrical insulation also presents significant impediment to removing heat from the stator conductors. Figure 6 shows the impact of groundwall thickness on the output capability.[76] Thus, the groundwall insulation of large form-wound generators and motors for which voltage endurance is pivotal and standards exist[77] is thus clearly a prime target application.
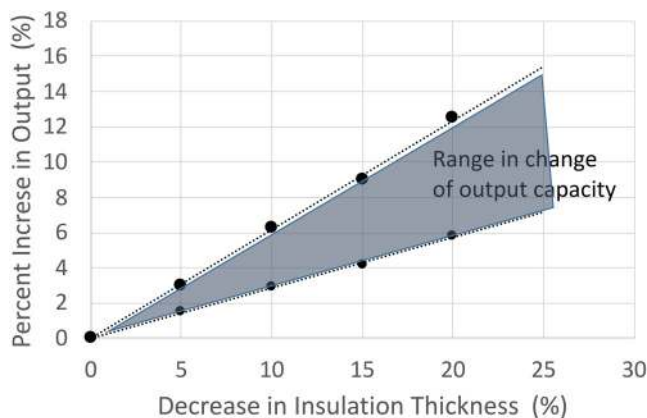
Extensive testing is needed together with experience with variables appropriate to the VPI (vacuum pressure impregnation) or resin-rich processing. Nevertheless, the potential gains appear so large that it is very likely that the industry will move in that direction. This may happen in stages. For example, there is no need to eliminate mica in favor of oxide nanofillers since, in the right circumstances, the latter may be used to good effect as an additional component.

One indication that the industry may introduce nanodielectrics is that many of the OEMs have in-house programs to study this although only a few are, understandably, publishing their findings. However, it is clear from Fig. 7 that full-size stator bars have been fabricated and tested with very encouraging results.[78] It appears that earlier laboratory results can, indeed, be replicated in full-size form-wound stator bars suggesting that some of the scale-up issues anticipated can be managed. From the viewpoint of machine insulation, in addition to enhanced voltage endurance, the salient advantages that can be expected from nanodielectrics may be summarized as follows:

- A small increase in the electrical breakdown strength (when compared with the equivalent base resin), but a substantial improvement when compared with a conventional (micro-sized) filled material. The improvements are usually more enhanced at elevated temperature, in divergent fields and with direct voltage.
- An increased resistance to erosion by discharges.[75]
- A reduced accumulation of internal space charge.[19,79]
- A modest, but useful, improvement in some mechanical properties.[80,81]
- A modest, but useful, improvement in service temperature.
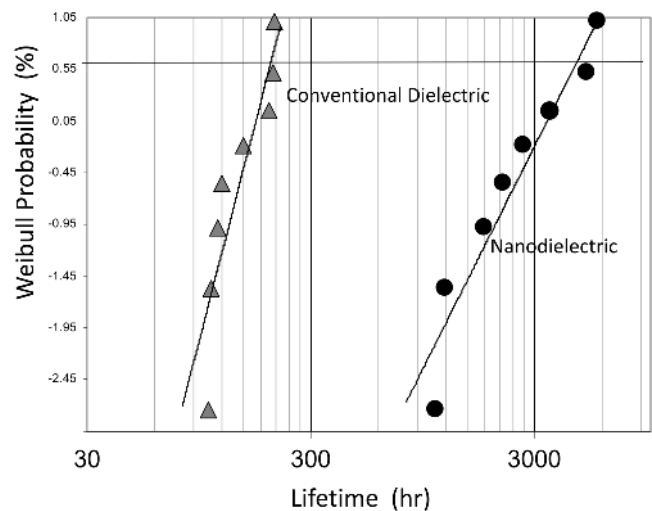- A modest, but useful, improvement in thermal conductivity.

FIG. 6. Impact of a reduction in groundwall in machine output.[76]

FIG. 7. Voltage endurance characteristics as a Weibull statistical plot for form-wound stator bars.[78]

B. Applications in wire enamels

The longevity of nanodielectrics under electrical stress could also have application in wire enamels. This combined with the often observed increase in resistance to erosion under stress[82] points to a means to develop corona-resistant insulating materials. In particular, small motors (and other devices such as solenoids) are typically designed using random wound conductors, which utilize enameled magnet wire. The insulation used will depend on the duty and temperature class and is often not required to be corona resistant because of the voltage class. However, the introduction of power electronic control with an inherent switching surge has increased the need for discharge resistant insulation. The use of high-temperature nanocomposites for this application is illustrated in Fig. 8 where wires coated with a formulation of alumina (Al_2O_3)–polyamideimide are subjected to a twisted-pair test.[83] The particle size was 40 nm at a 5 wt. % loading. The increased longevity under discharge is clear even at temperatures as high as 260 °C. The inset in Fig. 8 shows that the enamel after the discharge test (lower wire) is left coated with a white powder.

C. Capacitor applications

A review of the opportunities for nanodielectrics in capacitors has recently been provided by Streibl and Karmazin.[84] Key to success is increasing both DBS and permittivity. Thus, an obvious starting point is to form a capacitor dielectric from a base polymer such as poly(vinylidene fluoride) (PVDF) having a high permittivity. Wang et al.[85] have taken this approach using 25 nm copper phthalocyanine particles grafted onto poly(p-chloromethyl styrene). At a loading of 15%, a relative permittivity of 325 (at 100 Hz) was achieved, which represents a factor of nearly 40 improvement over the base polymer. High permittivity ferroelectric ceramic particulates, such as barium titanate, have also been the focus of attention by many[86,87] where it has also been possible to use surface modified $BaTiO_3$ to provide a greatly enhanced permittivity and
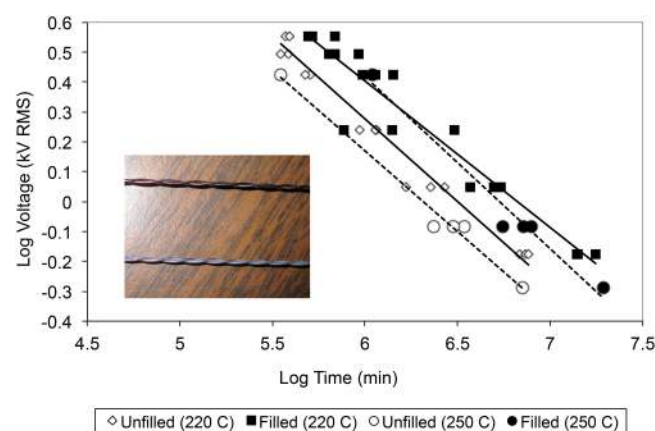

FIG. 8. Endurance data for unfilled and nanofilled composites in a twisted wire geometry with an image (inset) of the twisted wire after testing. The lines are a best linear fit.[83]

concomitant high electric strength. The addition of surfactants, such as phosphate esters may be undertaken to improve dispersion and more sophisticated ligand chemistry employed to minimize dielectric losses. Some of the approaches that can be adopted to improve nanodielectrics for electrical energy storage applications have been reviewed by Wang and Zhu[88] and often involve one of the controlled radical polymerization techniques.

Biaxially oriented polypropylene (BOPP) is also a candidate for improvement in properties using nanoparticles. Recent work has shown that a PMMA shell around a barium titanate particle in film polypropylene leads to a significant increase in both permittivity and breakdown strength,[89] and other works have shown that good dispersion of nanofillers in BOPP can lead to enhanced capacitance properties.[90,91]

Another strategy that has been explored is to depart from near spherical nanofillers and adopt a high aspect ratio approach. This has been investigated for barium titanate fillers prepared by electrospinning and solgel processing followed by heat treatment to form a perovskite crystal structure[33] and also by the use of graphene oxide (GO) platelets. Although the relative permittivity can be increased by this means, the local internal stress concentrations have been shown to have a deleterious effect on the dielectric strength making the strategy less attractive for capacitor applications.

VI. THE WAY AHEAD

Although the chemical functionalization of the nanoparticles started out as the result of needing to minimize agglomeration, it is clear from Sec. III that sophisticated methods have now been developed to introduce a wide variety of other molecular attributes that add functionality not native to the host polymer. As a result, not only is there interest in tailoring the surface of nanoparticles to enhance their properties but also to make them adaptive through the use of more than one population of surface ligands. A few examples are given here to illustrate.

A. Self-healing dielectrics

Electrical insulation that can undergo some self-repair after sustaining damage is clearly very desirable, especially when no external source is needed to bring about healing. It has been shown that mechanical repair can be achieved by encapsulated fluids that are released due to damage and locally cross-link the polymer.[92] Reed[93] has also documented examples where a measure of repair can be achieved in insulation systems. An example of this is the classic "clearing" phenomena designed into metallized film capacitors. Most damage in high-voltage insulation involves partial discharges, such as those that occur in voids, and is localized in nature. However, such discharges also involve photon *energy release* at exactly the place where healing is needed and can form the basis for a targeted self-healing strategy. Such a method was used by Sharbaugh and Shaw[94] in film–foil capacitors but required intervention by the use of a unsaturated plasma-polymerizable gas (e.g., vinylidene fluoride or acrylonitrile) to lay down new polymer and increase the discharge inception voltage.

In contrast, the incorporation of nanoparticles provides a vehicle for the introduction of active elements at the large internal surface of the polymer matrix. Furthermore, if those active agents

are photosensitive, then they can utilize the energy generated by light emission processes in dielectrics. This light may be the result of tree channel development, partial discharges, or possibly, electro-luminescence created by the downward transition of excited electrons or by recombination. The energies involved with such plasmas can be as high as 40 eV (electrons 0–20 eV, ions 0–2 eV, metastables 0–20 eV, and UV radiation 3–40 eV). This forms a basis for the choice of an active moiety to initiate some repair by a variety of pathways. This is an active field[95] but with little application to high-voltage dielectric structures. However, much of the chemistry identified and the principles expounded may be considered for electrically insulating materials, and several approaches to self-healing, which can harness the plasma energy, can be identified:

1. It can be a cross-linking agent to provide a measure of healing in the existing polymer. This has been demonstrated[96] for an epoxy-SiO$_2$ nanocomposite using the methods outlined in Sec. III to provide a grafted block copolymer with a plasma reactive inner block, polydimethyl siloxane (PDMS), and a compatible outer block. In this way, the methacrylate groups of the monomer were polymerized leaving the PDMS side groups available for cross-linking[97] to create the desired self-healing measured by substantial reductions in partial discharge magnitude and enhancements in lifetime.
2. Grafting plasma-polymerizable material may be employed to introduce a new polymer.[71]
3. It can be a chromophore to generate temperature activated self-healing or local heating and thus some melting of the existing polymer. Nanoparticles and chromophores absorb light over a range of wavelengths, and their absorption cross sections can be tuned both for one- and multi-photon absorption. The only molecular moieties likely to absorb light in the 200–800 nm region are π-electron functions. Molar absorptivity may be very large for strongly absorbing chromophores. The magnitude reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.[98] This has advantages over some previous methods, such as the incorporation of magnetic or resistive particles to bring about heating, which are likely to negatively impact the dielectric properties.
4. It can utilize a photo-reactive element that creates local conductivity to redistribute stresses or even "short out" partial discharge cells.
5. The use of a functionalized photoresponsive moiety such as azobenzene brings about an intrinsic healing mechanism triggered by UV-induced $trans \rightarrow cis$ isomerization of the azobenzene chromophore, which enables the damaged polymeric matrix to recover.[99] Furthermore, morphological changes accompanying photochromism can also be achieved.

Note that it is evident that some of these mechanisms will be less applicable in thermosets because of limited chain mobility.

B. Stress-grading nanocomposites

The techniques needed for designing industrial insulation structures often involve the mitigation of electric stress by the choice of geometry or material combinations to redistribute the electric field.

However, there are limits to these choices and the incorporation of surface coatings, screens, and non-linearity may be needed in order to accommodate high potentials in the requisite space. Nanodielectrics can be engineered to exhibit highly non-linear conductivity so as to automatically relieve the structure of electric stress when a threshold is approached. This may be achieved through the use of non-spherical nanoparticles.

As an example, graphene oxide (GO) has a platelet structure and abundant surface groups having hydrophilic characteristics allowing for easy dispersion in the form of single layer platelets. GO can be reduced by either chemical or thermal methods to control the conductivity. Consequently, the electrical properties can be controlled by adjusting the oxidation states. If a slightly thermally reduced nanocomposite is formed with poly(dimethyl siloxane) (PDMS), Fig. 9 indicates that an unusual nonlinear (coefficient = 16) electrical conductivity can be achieved for a filler loading of only 3 vol. %.[100] From the application point of view, the conductivity saturates beyond the switching field, which avoids the overheating typically seen in commercial field grading materials. Both the switching field and saturation conductivity can be adjusted through the loading and the GO oxidation state.

In general, layered systems seem to be able to achieve what bulk systems cannot, and there has been recent development work undertaken[101,102] in functionally graded materials (FGM) employing nanometric particles both to change electric field distributions through permittivity (ε-FGM) or conductivity (σ-FGM),[19] depending on the nature of the applied stress. In this way, the electric field in critical areas such as triple-point junctions can be made more homogeneous allowing the insulation to be used more effectively. This involves the introduction of nanoparticles having the required properties in such a way that they can be spatially distributed non-uniformly in the bulk by centrifugal forces or by sedimentation (gravity-assisted casting). This technique may be refined by using
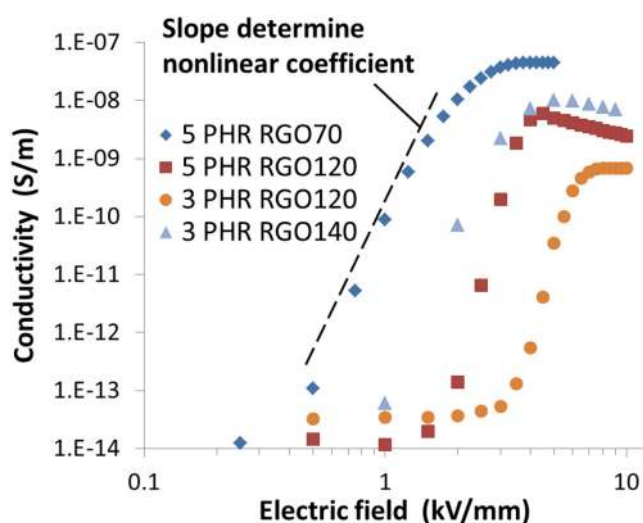

FIG. 9. Plot of conductivity as a function of electric field for a PDMS/GO nanocomposite showing the effect of loading and of reducing GO at different temperatures.[100]

two species of nanoparticles having different properties and dimensions so that localization can be controlled by the centrifugal forces applied. ε-FGM has been applied to the disk spacers used in gas-insulated utility substations, and a 12% advantage has been observed.[101]

C. Self-organizing systems

It was recently demonstrated that through careful control over the crystallization rate, nanoparticles can be organized between the lamella in low molecular weight polyethylene leading to a sheet like structure of nanoparticles (Fig. 10).[103] Given the impact of layered systems on dielectric breakdown strength that are formed *ex situ*,[104] *in situ* formation of layered systems could lead to the ability to create large-scale systems with this structure. The impact on the cable industry and others that take advantage of semicrystalline polymers could be game changing. This is just a small example of the many ways in which block copolymers and other carefully tailored nanofillers can be organized quickly (Fig. 10) and

efficiently into materials with intriguing properties.[105–107] The nanodielectrics community would need to tailor these approaches for appropriate materials systems, but there is likely much to be gained from doing so.

D. Rational materials design

As this article makes clear, the complexity in nanodielectrics makes it difficult to identify mechanisms, model behavior, and design the next material. The physical phenomena that occur during breakdown span the length scale from atomic scale to micrometer scale avalanche-driven breakdown. While the community is working to develop multiscale models,[108–110] it is a challenging problem. One way to develop physics-based multiscale models, upon which a materials design approach can be adopted, is to use larger datasets to develop empirical informatics models that help bridge the length scales.[111] To do this, there is a need for a data resource that captures the data, metadata, and
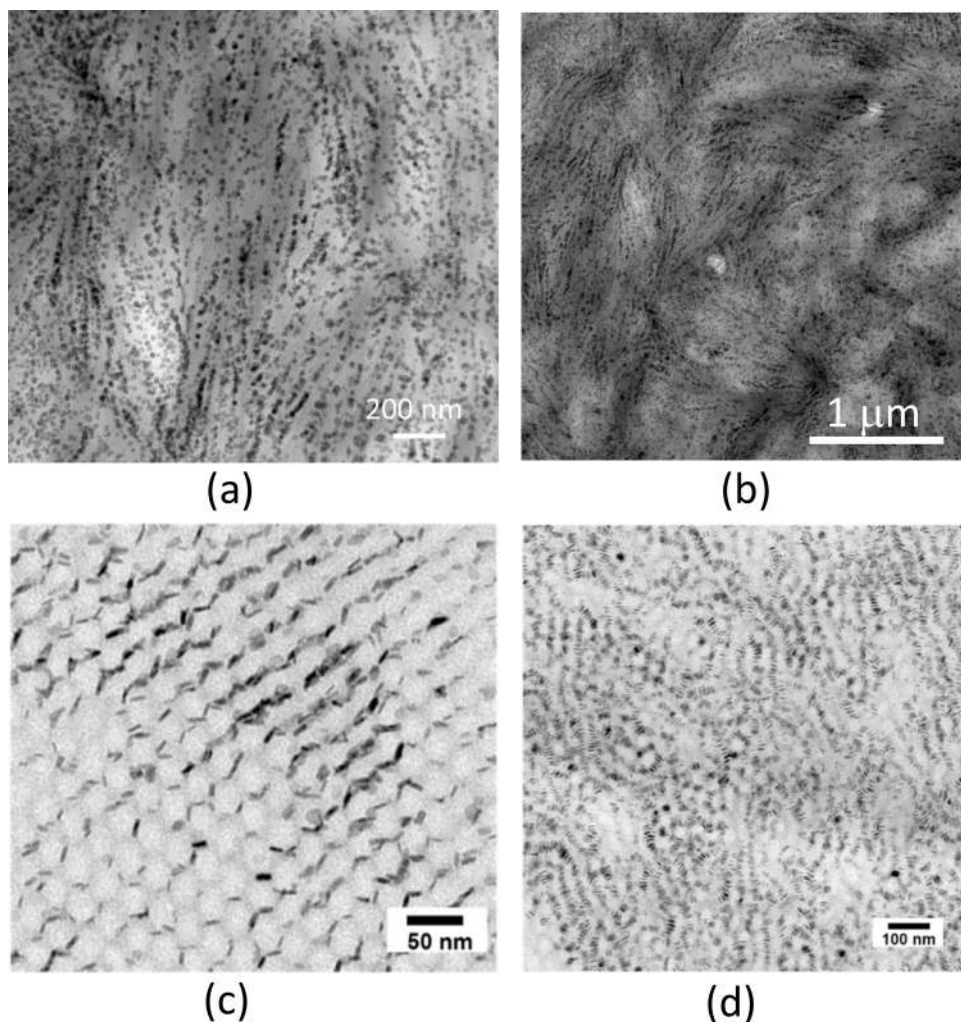

FIG. 10. Examples of self-organizing nanofillers. (a) and (b) Nanoscale silica in polyethylene at two magnifications,[103] and (c) and (d) copper sulfide nanodisks in block copolymer at two magnifications.[105]

dispersion information. There is a nascent resource, NanoMine,[112] which is leading the way.

In addition, using a materials genome approach[113] toward the development will be important. The work by Mannodi and Ramprasad in which they have identified clear trends between bandgap and dielectric constant, for example, has led to identifying new polymer systems (Cd or Sn containing polymers) with significantly higher dielectric constant. While these techniques are more straightforward (though not easy) for polymers than for two and three phase systems, it is critical that we start to look at such strategies seriously and respect the insight they provide as a compliment to multiscale models that try to capture the detailed physics.

There have been some recent attempts in this area,[114–116] and just as a design-based approach was critical to the use of fiber based composites in high-end applications (such as aircraft), a similar approach will be necessary before they will be used in applications for power transmission. It will require more data on lifetime behavior, environmental effects, and including those behaviors in the modeling and design approaches. This field has incredible promise. The organizations and companies that invest in developing the full scale approach to design using all the new tools available will ultimately have a product that is unique and superior to the rest.

VII. SUMMARY

In summary, nanodielectrics are an exciting field, but the barriers to commercialization are large and require significant focus in several key areas:

1. Some specifications by the community about reporting on, and quantifying, filler dispersion.
2. A data resource that brings together the available literature, and the subsequent multiscale models and design approaches that can result.
3. Investment in studying the aging behavior and the methods for scale-up.
4. A risk averse set of companies to scale-up tailored filler surface modifications, composite processing, and large-scale testing of nanodielectrics as part of components.

While the literature already suggests a promising class of materials, there are ideas still emerging on how to organize particles at scale, combine types of particles, create self-healing materials, and more that suggest that this field is still nascent and ready for further revolutionary impact on a host of fields.

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DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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