

50th Anniversary Perspective: Are Polymer Nanocomposites Practical for Applications?

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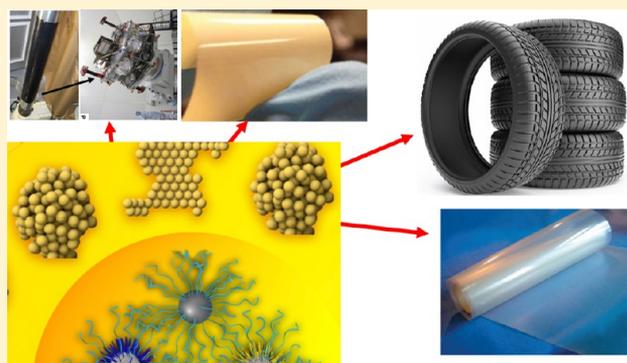
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ABSTRACT: The field of polymer nanocomposites has been at the forefront of research in the polymer community for the past few decades. Foundational work published in *Macromolecules* during this time has emphasized the physics and chemistry of the inclusion of nanofillers; remarkable early developments suggested that these materials would create a revolution in the plastics industry. After 25 years of innovative and groundbreaking research, PNCs have enabled many niche solutions. To complement the extensive literature currently available, we focus this Perspective on four case studies of PNCs applications: (i) filled rubbers, (ii) continuous fiber reinforced thermoset composites, (iii) membranes for gas separations, and (iv) dielectrics for capacitors and insulation. After presenting synthetic developments we discuss the application of polymer nanocomposites to each of these topic areas; successes will be noted, and we will finish each section by highlighting the various technological bottlenecks that need to be overcome to take these materials to full-scale practical application. By considering past successes and failures, we will emphasize the critical fundamental science needed to further expand the practical relevance of these materials.



INTRODUCTION

Polymer nanocomposites (PNCs) typically contain one or more nanoparticle (NP) components within a polymer matrix. While these hybrid materials have been studied from the 1940s with a particular focus on rubber tires, this area was reinvigorated in the 1990s when platelet-like clay particles¹ were exfoliated in a range of polymers—first into semicrystalline and later into amorphous polymers and networks. For example, researchers at Toyota Central Research showed that less than 5 vol % of exfoliated montmorillonite in nylon-6 increased the modulus by a factor of ~3, while at the same time increasing the heat deflection temperature from ~340 to ~420 K.² These demonstrations inspired the community to understand how to cost-effectively disperse nanoscale sheets, rods, or spheres into polymers and resins. In parallel, others focused on determining the crucial physics that led to an enhanced

thermomechanical property suite without concomitant degradation in strength, toughness, or processability.

Pioneering work published in *Macromolecules* during this time emphasized the physics and chemistry of the inclusion of inorganic and organic nanofillers, including spherical nanoparticles (e.g., silica, titania, C₆₀, etc.),^{3–8} carbon nanotubes,^{9–13} clay,^{14–22} graphene,^{23,24} metal nanowires, nanorods, and quantum dots into a range of polymers. Because of the scalability of the early synthesis and processing approaches, many felt that these concepts would be the foundation of a revolution in the plastics industry, where new resin lines would

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be based on judicious formulation of existing resins and nanofillers.

While over 25 years of innovative PNCs research have yet to produce this broad plastics revolution, PNCs have provided many valuable niche solutions. PNCs are now a billion-dollar global industry with products ranging from reinforcing components for the transportation industry to commodity plastics with enhanced electrical properties for shielding and electronics. Rather than NP addition altering fundamental polymer characteristics, many of these successes are based on the NP adding functionality without degrading polymer processability. These successes are still inspiring academic and commercial research toward new applications^{25–27} as well as establishing the critical underpinning science. A large number of excellent review papers (e.g., for clay-based materials^{28–33} and carbon nanotubes composites⁹) and books^{31,34–36} are available that chronicle and summarize the status of various nanoparticle–polymer combinations.

The original questions formulated 25 years ago nonetheless remain—some fundamental and some more practical. To what extent can the basic characteristics of polymers be altered by the addition of NPs that have at least one dimension comparable to the macromolecular size? Developmentally, what is the extent of the novel property suites that emerge from this synergism, and can it be utilized through the engineering of the morphology and characteristics of the polymer–nanoparticle system (namely particle size, chemistry, the functionalization of the particle surface, matrix chain length, matrix chemistry, etc.)? Practically, are the synthetic and processing innovations required for the requisite control of NP–polymer miscibility and assembly commensurate with cost-effective scale-up and manufacturing?

Two crucial PNC concepts developed early on are worth stressing here. First, the PNC “effect” is generally ascribed to the reduction in filler dimension; that is, in going from colloidal, micrometer-sized fillers to NPs leads to a 10^6 increase in surface area, i.e., that the surface-to-volume ratio increases dramatically, and magnifies the importance of interfaces. The impact of this PNC effect, however, is not uniform across physical properties. For example, polymer–NP coupling impacts viscoelastic and thermomechanical response in a fundamentally different way above and below T_g .^{37,38} Further, the relative importance of the composition and structural characteristics of the interface varies widely; the interface impacts conductivity, dielectric breakdown, permeability, optical transparency, etc., in disparate manners. Thus, the development of a universal concept for PNC interface engineering has been extremely challenging. A corollary to the increase in interface is the decrease in interparticle distances, such that at even modest NP concentrations this characteristic distance is comparable to the radius of gyration of polymers. This can influence polymer conformations^{39–41} and properties, and as an example, a recent *Macromolecules* Perspective captures the impact on polymer center-of-mass diffusion.⁴²

The second concept is the impact of the commensurate length scales between the physics determining polymer properties and the hierarchical morphology of the NP phase. For example, mechanical reinforcement of an elastomer may be engineered through the percolation of a network with the NPs as the nodes and the chains as the bridges.^{11,43–66} Likewise, enhanced toughness may be engineered by energy dissipation at these interfaces ahead of the crack tip. Also, maximum

electrical conductivity depends on simultaneously driving percolation but affording NP–NP surface contact.^{67–75} Therefore, the optimal PNC morphology for given physical properties is not necessarily maximum uniform dispersion (well-separated). In many cases, hierarchical control of the distribution of NPs is key, that is, tuning morphology from a uniform nanoscopic dispersion to a range of self-assembled structures such as strings, sheets, cellular structures, etc.^{76–83} Such architecture-dominated phenomena become particularly accessible when the NPs and polymer chains are comparable in size, leading to behavior not found in colloidal or unfilled macroscopic analogues. However, such fine control of miscibility, structure, and architecture has proven very challenging, especially with respect to also addressing the complexity of optimizing the interface for the mechanical–electrical–thermal–processability–performance suite required for a given technology.

To complement the extensive literature currently available, we will examine four case studies of PNCs applications, i.e., their proposed or actual use. Our goal is to understand why PNCs have become practical for some but not (yet) for other applications. Our choice of applications is somewhat arbitrary, but we chose to highlight one highly successful application where improvements are still desired, one successful niche application, one which has potential application, and a last one that has not yet found an application niche even after a couple of decades of research. In particular, the platforms that we discuss are (i) filled rubbers (commodity material), (ii) continuous fiber reinforced thermoset composites (niche application), (iii) membranes for gas separations (potential exists), and (iv) dielectrics for capacitors and insulation (limited applications). A central question that underpins all of these topics is the dispersion state of the NPs in the polymer matrix, how it can be controlled in a facile manner, and most importantly how lab-scale ideas can be scaled up to industrially relevant processes. Controlling this dispersion state then is central to the ready applicability of PNCs to a suite of existing and future applications of these materials.

In this paper, we begin by presenting synthetic developments, which underpin progress in this field. Given the critical nature of the NP dispersion state in the polymer, we have a brief discussion of this topic and the experimental methods used to detect it. We then discuss the application of polymer nanocomposites to each of these topic areas; successes will be noted, and we will finish each section by highlighting the various technological bottlenecks that need to be overcome to take these materials to full-scale practical application. By considering past successes and failures, we will emphasize the critical-path fundamental science needed to further expand the practical relevance of these materials.

■ FOUNDATIONAL PAPERS

Twenty-six of the most cited papers published in *Macromolecules* over the past two decades^{3–5,7,8,10,11,13,15–23,47,67,84–90} are representative of the broad-based progress that has been achieved on this topic. These papers span all the way from theory, synthesis, *in situ* functionalization of NPs during processing, rheological effects, and several review articles. The review below is inspired by many of these papers, while at the same time not duplicating these efforts.

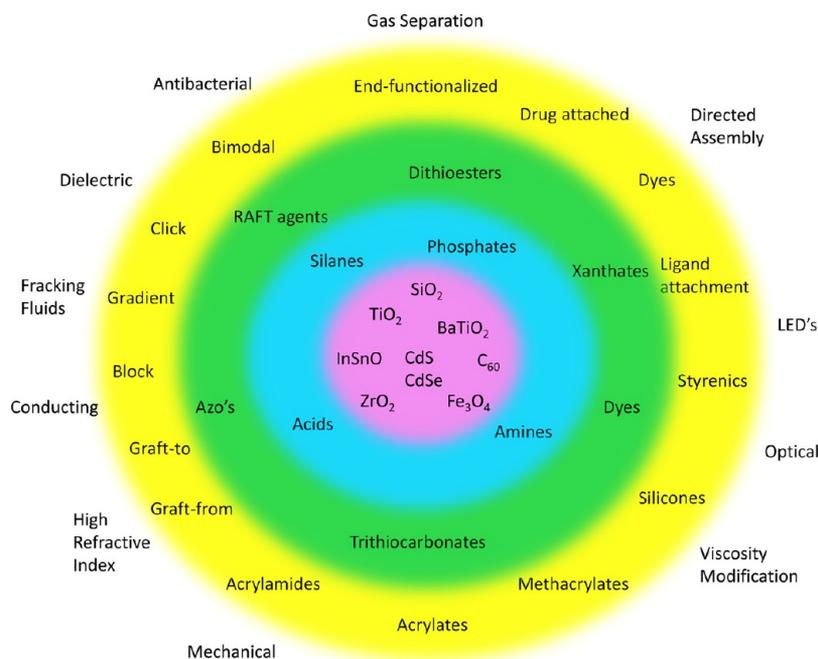


Figure 1. Schematic illustration of the various types of NP available, the forms of surface functionalization, and the applications that these materials can impact.

■ SYNTHETIC DEVELOPMENTS

It is now clear that the interface between a NP and the surrounding polymer matrix plays a critical role in determining the dispersion state, organization, wetting, chain dynamics, and ultimately many of the properties of a polymer nanocomposite.⁹¹ Thus, the demands to control many aspects of the chains attached to (or in association with) the particle surface have grown over the past few decades, which presents many challenges and opportunities for synthetic polymer chemists. In this same time frame, the discovery and development of controlled radical polymerization methods (atom transfer radical polymerization (ATRP),⁹² reversible addition–fragmentation chain transfer (RAFT),⁹³ macromolecular design via reversible addition–fragmentation chain transfer (RAFT)/xanthates, and nitroxide-mediated polymerization (NMP)⁹⁴) were quickly adapted to exercise control over polymers attached to NP surfaces.^{95–103} The correlation between changes in chain placement or chain length on the dispersion state has driven home the importance of this local environment on properties.¹⁰⁴ Experience has shown that simultaneous control over many molecular variables of the grafted chains, i.e., chain density, chain length, chain dispersity, molecular architecture, etc., is necessary to understand and optimize the dispersion state, strength of interaction, and resulting properties.¹⁰⁵ Grafting-to and grafting-from approaches have both been useful in creating specific interfaces and are applicable in different graft density ranges.^{106–111} The limitation of the grafting-to method is the steric constraint of attaching polymer chains to a substrate surface.^{112,113} The initial population of polymer chains establishes a surface, and it becomes increasingly difficult for new chains to diffuse to the NP surface and attach.¹¹⁴ Thus, grafting-from methods are required when higher chain densities are preferred (0.01–0.8 chains/nm²). Figure 1 illustrates the various NPs chemistries, the different surface functionalization strategies adopted to

date, and the fields that these NPs are expected to be relevant in.

The general strategy for grafting-from inorganic metal oxides is to react the inorganic particle surface with a “coupling agent” to essentially convert the inorganic surface to one of organic reactivity.¹¹² Then, many subsequent organic functional group interconversions can be conducted to the desired functionality. In the most common case, silica surfaces are reacted with silane coupling agents to create organic surface groups such as –OH, –COOH, –NH₂, and –CH=CH₂.^{100,111,115} These can then be reacted with ATRP, RAFT, or NMP compounds that also contain a complementary reacting group.¹¹³ Controlled radical polymerization (CRP) agents have been developed which contain both the controlling agent and surface reactive groups in the same molecule.^{99,116–118} Azo initiator groups have also been attached to NP surfaces.¹¹⁹ This approach allows for the polymerization of many common monomers as well as functional monomers or click monomers and careful control over the placement of such functionality using block copolymerizations.^{120–122} Steric constraints associated with the grafting-to approach are minimized since the monomer can easily diffuse to the surface to access the propagating chain ends.

Many types of NP have been modified using these approaches, including titania,¹²³ silica,¹⁰⁰ barium titanate,¹²⁴ indium tin oxide,¹²⁵ zirconia,¹²⁶ iron oxide,¹²⁷ CNTs,¹²⁸ and others.¹¹² The coupling agents need to be chosen judiciously to provide sufficient reactivity with the nanoparticle substrate. Silane coupling agents have been developed for many years but are less reactive with some metal oxides. Phosphate/phosphonate, carboxylic acids, and amine-based ligands have been used to complement silane coupling agents.¹¹³ Thiol–gold bonding is widely used to functionalize gold nanoparticles, but care should be exercised in applications where an aggressive environment or high temperatures are present.¹²⁹ The weaker nature of the gold–thiol bond (30–50 kcal/mol) may

substantially change the grafted environment in such conditions via loss or rearrangement of grafted chains.¹³⁰

More recently, ligand engineering of surfaces has been extended to bimodal grafting strategies to separately optimize the enthalpic and entropic components of mixing.^{131,132} In a typical approach, a densely grafted, short brush is polymerized from the surface to screen the enthalpic core–core attraction between two NPs, which can otherwise lead to agglomeration. A subsequent sparsely grafted long brush is polymerized to enable these chains to manipulate the entropic effects associated with the mixing of the matrix and the grafts.^{132–134} Both theory and experiment have shown this approach to be superior in controlling the dispersion of NPs relative to the monodisperse analogue. In one demonstration of this approach, the dispersion of titania, well-known for aggregation and scattering light to make polymers “white”, was accomplished even at high titania loadings resulting in clear composites, with obvious applications in high refractive index materials such as LEDs.¹³⁵ Apparently, control of multiple molecular variables (chain density, molecular weight, dispersity) can be attained on two separate chain populations, both simultaneously and independently. However, many more opportunities exist if this concept is extended generally to multimodal or multifunctional populations of ligands.¹³¹ After selection of a nanoparticle with its own inherent property (high surface area, high refractive index, magnetic properties, etc.), we can then choose a variety of groups and chains to place on the surface to control matrix compatibility, thermal or pH responsiveness, color, photosensitivity, field effects, or biological activity. Alternatively, a set of NPs each with a distinct surface functionality can be incorporated into a single PNC. This type of ligand engineering is just beginning to be explored and will be a focus of synthetic developments for targeted applications.

NP DISPERSION

As discussed above, there have been many pioneering contributions to the use of surface ligands on nanofillers to tailor the enthalpic and entropic driving forces leading to assembly of these polymer-grafted NPs in amorphous polymer matrices/melts, characterizing the resulting NP structures and understanding their consequences on properties, and delineating the theoretical bases for the observed NP spatial distribution and properties.^{60,133,135–143} Figure 2 shows that we can use thermodynamic principles to predict the morphology (strings, sheets, or spherical agglomerates) that will develop for a given graft density and brush/matrix molecular weight ratio. It has also been shown that by using a bimodal population of brushes (high graft density of short brushes and a low graft density of long brushes), we open up the window for creating well-dispersed fillers. How these equilibrium ideas are affected by processing conditions is central here. Recent work by Moll et al.¹⁴⁴ suggests that the application of shear tends to break down self-organized nanoclusters. In contrast, Vermant and co-workers showed that colloidal size particles can be driven into ordered states through the application of external shear.¹⁴⁵ How processing affects NP assemblies is thus an open topic that is worthy of investigation, especially since certain structures are particularly useful in enhancing the mechanical and electrical properties of the resulting composites.

While TEM is typically used to “visually” characterize NP dispersion, this is not an accurate means to determine this important quantity. Rather, scattering tools (small-angle X-ray/

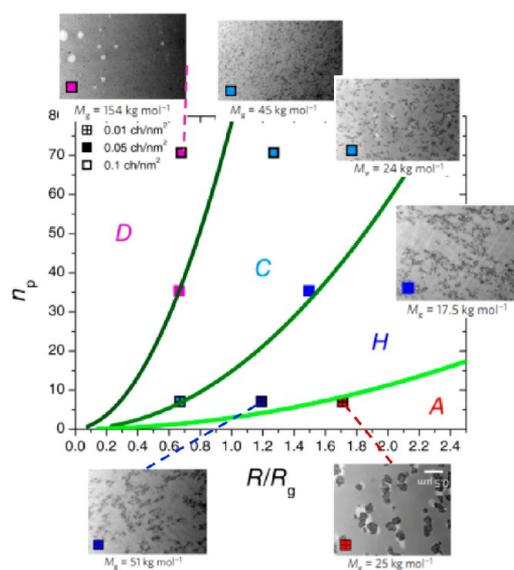


Figure 2. Map of the grafting density vs the ratio of the NP size and chain radius of gyration. A = amorphous aggregates, H = sheets, C = chains, and D = dispersed NPs. Adapted from ref 132.

neutron scattering) are the most appropriate means to characterize dispersion. In the limit of low NP content, the scattering curves typically show a sharp increase at low q (the scattering vector) when the NPs are phase separated (or agglomerated into large structures). A plateau at low q then characterizes well-dispersed states. Even here, the absolute value of the plateau of the structure factor, which can be derived from the scattering data, immediately yields the mean number of NPs in local clusters (the clusters are still well-dispersed in the melt). Larger NP concentrations then need the structure factor to be described by an appropriate model, such as the Percus–Yevick hard sphere model, but the essential point is that we can describe the spatial dispersion of NPs from the local single NP level to the formation of larger structures. We refer here to the many works in this area, in particular, the work of Jouault, Jestin, and co-workers, for more details.^{146–153}

APPLICATIONS

Filled Rubbers. Probably the most ubiquitous application of nanofilled polymers is in the context of rubber tires,^{3,44–46,48,53,154–169} and these have well-established performance metrics that need to be considered in the context of applications. First is the need to decrease the rolling resistance of a tire, while keeping its wear resistance high. Similarly, wet traction is an important issue. All of these features have to be considered in tire design, while, at the same time, keeping the tire’s weight and cost under control. The tire industry (e.g., Michelin and Bridgestone) has used carbon black and colloidal silica as fillers in their tires, and a considerable amount of work has illustrated that an improved particle dispersion in the cross-linked rubber is key to improving properties. Couty (Michelin)^{153,170} has shown that “breaking down” NP agglomerates into smaller entities during industrial processing is critical to improving mechanical properties. Achieving this improved uniformity within the framework of current processing protocols then remains the outstanding challenge.

The research literature in this community is vast, spanning many decades, and emphasizes several key points. First, the formation of a “bound” polymer layer (including chains bound

through chemical interactions, Figure 3) is a central focus.^{166,167,171} In particular, several workers have postulated

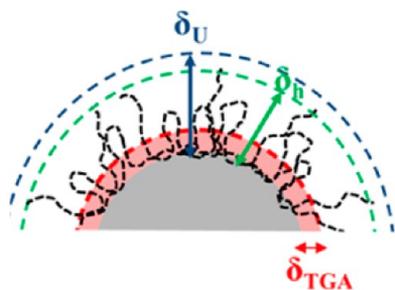


Figure 3. Schematic illustration of the presence of a bound layer and a layer of intermediate mobility in a filled elastomer. From ref 174.

that a bound layer is critical in determining mechanical reinforcement.^{63,160,172–174} While there have been many studies, the factors determining the formation and the size of this bound layer remain unclear. Second, the mechanical reinforcement in these cases is attributed to NPs and how they interact with and modify the polymer network. How the NPs affect phenomena such as the Payne effect have also been focused on. The Payne effect corresponds to the strain amplitude dependence of the viscoelastic stress in a filled rubber, and it is now well accepted that the polymer–NP interaction plays a central role in this case.^{45,46,156,162,175} Again, the role of the bound layer on the mechanical behavior remains unresolved. Underpinning all these effects, and the topic of continuing focus, is how the NPs are dispersed in the matrix and how these dispersions are affected by the processing scale (i.e., small samples in the lab vs industrial mixers). The effects of particle agglomerates (vs individually dispersed NPs) on properties are not properly enunciated.¹⁷⁶ Similarly, since ideas of controlling NP dispersion derived in the lab do not scale up properly to the industrial scale, this issue continues to be the central focus of research in this area.

Another relevant application is in filled epoxies, which typically have high T_g values (much greater than room temperature).^{177–179} Epoxy resins are regularly used in high-performance applications, e.g., coatings and adhesives. Typically, an adhesive is applied between a silicon chip and a substrate to ensure that the joint is not stressed due to a mismatch in their coefficients of thermal expansion. The brittle nature of epoxy resins can be mitigated through the use of NP fillers. However, these additives always result in trade-offs. For example, if fracture toughness improves, then there is a reduction in yield stress or the elongation to break. Similarly, Thomas et al.¹⁸⁰ find that the mechanical reinforcement of epoxy networks goes through a maximum with copper oxide NP loading at about 2.5 vol %. Apparently, the NPs begin to agglomerate at higher concentrations, leading to worsening performance. Recent work by Maillard et al.³⁸ suggests that the addition of grafted NPs can help to increase the Young's modulus, yield stress, and strain to failure. While this previous work was in the case of glassy, un-cross-linked polymers, we believe that comparable ideas should carry over to the case of cross-linked glassy epoxies. What are the conditions under which these simultaneous improvements in properties be achieved?

There are important questions that remain to be addressed in this comparatively mature field of PNC research/application.

First, what is the best NP dispersion state for optimizing mechanical properties? Is it a well-dispersed NP state, as assumed by many in the rubber community, or does a fractal percolating structure optimize mechanical reinforcement as found in thermoplastic melts?⁶⁰ Does the same dispersion state maximize rolling resistance, wear, and wet traction? If not, what is the NP dispersion state or combination of states that best optimizes these properties? What are the properties of the filler that are optimal? Should the filler be spherical or some other shape (including fractal objects like fumed silica)? Or what is the correct distribution of shape and size of fillers, including blends of different nanofillers? What is the role of the bound polymer layer? Does it need to be glassy to maximize mechanical reinforcement? What controls the Payne effect, and what is the optimal NP–polymer interaction strength in this context? Under the assumption that we can determine the optimal NP dispersion state, what processing protocols do we need to achieve this target morphology? Can we continue to use the current processing protocols but design nanoparticles, polymers, and process variables to achieve these goals? What is the role of theory here? Can detailed atomistic models shed light on the creation of the bound layer, whether it is physically adsorbed or if chemical changes occur? How do these bound layers mediate the interactions between the NPs and thus lead to the properties of interest such as the wear resistance, rolling resistance, and the Payne and Mullins effects.

Continuous Fiber Reinforced Composites (CFRCs). Continuous fiber reinforced composites (CFRCs) are the archetype of an engineered system of materials. From glass fibers in the 1940s to carbon and aramid systems of the 1960s, CFRCs are the basis of technologies spanning aerospace to transportation, renewable energy, and sport. The morphology of the fiber, the matrix, their associated interface treatments, and their relative arrangement are designed to optimize a unique set of performance-cost requirements demanded by specific parts, such as panels, stiffeners, face sheets, vessels, tubular struts, and joints. Current engineering tools enable the designer to minimize failure modes, such as delamination, compressive matrix failure, fiber buckling, or fiber pull-out. Over the past five years, NPs and PNCs have become another tool in this design toolbox. Rather than replacing CFRCs with PNCs, they are being integrated into the overall composite system as an additional constituent. The resulting property improvements are utilized to forestall failure modes, offer lower cost processing, impart additional functionality, or provide a lighter weight design.¹⁸¹

As an example, consider the mechanical limits of CFRCs during flexure. The mechanical properties of the thermoset matrix have a primary effect on the composite's compressive strength and resistance to interlaminar cracking. The stiffness of the matrix affects the CFRC's compressive strength because fiber microbuckling, a major compressive failure mechanism, depends on the amount of support provided to the fibers by the matrix. The fracture resistance of the matrix, along with adequate fiber–matrix interface strength, is important in resisting interlaminar cracking within the CFRC. The conflicting requirements for high matrix stiffness and fracture resistance generally force compromises, which lead to design limitations in structural elements such as panels and tubes with high aspect ratios. Initial developments of nanocomposite thermosets focused on high aspect ratio nanoparticles such as nanoclays,^{182–184} CNTs,^{9–13} and more recently graphene.^{23,24,185} Generally, these systems showed 10–35% improve-

ment in mechanical properties with 0.2–5 wt % filler. However, the translation of these improvements to prepegs or laminates proved to be difficult due to processing issues, including extremely high viscosity, NP filtration, NP agglomeration, and void formation. Recognizing that enhancements of the resin's compressive modulus alone could deliver CFRC performance gains in select applications, such as high-aspect ratio structures requiring flexure, a team at 3M built on prior studies on nanosilica dental materials to develop a silica-based nanocomposite resin technology.^{186–189} Simultaneous optimization of surface modification and processing techniques afforded high volume fractions (up to 45 wt %) with minimal viscosity change that maintained the ability for fiber infusion (Figure 4). Also, the substantial volume reduction of organic matrix reduced water absorption and thermal expansion.

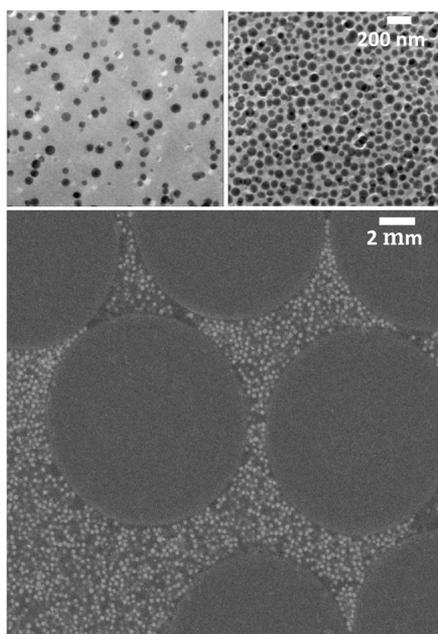


Figure 4. The 3M nanosilica matrix resin. (top) TEM micrographs demonstrating the range (15 and 45 wt %) of uniform dispersion of nanosilica in epoxy. (bottom) SEM image of a polished carbon fiber composite cross section showing the distribution of the nanosilica. Adapted with permission from ref 187.

Even though elongation to failure decreased (2% to 1.5%) and resin density increased, this specific set of property enhancements expanded the design space such that these resins improved overall CFRC performance. For example, G-Lumous used this technology to manufacture fishing rods with a 30% reduction in mass and 30% increase in load to failure, all while maintaining the deflection properties of the original design.

Similar nanocomposite thermosets based on higher performance resins, such as cyanate esters, are currently under development for aircraft and space applications. This general concept of using spherical nanoparticles to balance performance and inorganic volume fraction with processability was also the basis for the Lockheed Martin's nanofilled silicone "shuttle tile repair kit" carried on each space shuttle mission. The controlled viscosity resin provided ablative performance equivalent to shuttle tiles for repair of damaged shuttle tiles in orbit.

Adding multifunctionality to the CFRC provides another example of the impact of PNCs and emphasizes opportunities

afforded by novel PNC processing approaches. Although blends of polymers and conductive nanofillers, such as CNT^{10,190} and graphene,^{23,185} exhibit conductivities adequate for electrostatic discharge and electromagnetic interference shielding, the aforementioned processing issues as well as surface finish and dielectric heterogeneities limit their direct use as high-performance composites. However, the development of conductive nanoparticle veils, such as Ni nanostrands (Conductive Composites) and CNT paper (Nanocomp Technologies, Inc.), and the subsequent demonstration of resin infiltration, has provided a resin-agnostic approach to conductive nanocomposites that is compatible with composite lay-up processing (Figure 5). These NP-based veils provide an example wherein NP dispersion is not required for property improvements, specifically for electrical conductivity. For example, the Juno spacecraft, which recently entered orbit around Jupiter, incorporated a surface layer of CNT paper on several critical components of the flight system's attitude control motor struts and the main engine housing to provide protection against electrostatic discharge.¹⁹¹ Compared to alternative technologies, such as bonded Al film, the CNT fabric and its compatibility with composite manufacturing process offered cost and schedule savings by eliminating the labor-intensive surface preparation steps for composite surfaces. Also, these resin-infused CNT sheets were lower density than prior aluminum foil technology and provided >50% mass savings in the outermost layer of composite. Incorporation of other NPs in fabrics and veils to facilitate CFRC processing is expanding, such as for the development of conformal and graded ablaters. Early work demonstrated the self-passivating character of PNCs when exposed to extreme environments, such as fire, space, and rocket exhaust.^{192–194} Current nanomodified phenolic and silicone based ablator and insulator layers are undergoing evaluation by NASA for super lightweight thermal protections for several re-entry systems.

The use and impact of PNCs in CFRCs has been predicated on the balance of processing with performance. Unfortunately, the relationship between NP structure (size, shape, surface functionalization) and the complex chemorheology of nanofilled thermosets is still limited, especially with respect to the confines of a superstructure (fiber tow, weave, fabric, or veil). Innovative concepts to incorporate nanoreinforcements adjacent to the fiber, such as via sizing or coatings, or between plies, such as via *in situ* spraying, have the potential to significantly improve the shear and tensile properties of these interfaces and thus reduce delamination and offer more robust and lightweight primary structures and joints. As for materials, the inherent brittle nature of the thermoset matrix is a universal challenge. Mitigation via the use of viscoelastic additives always introduces trade-offs, such as reduced stiffness for increased toughness. The use of spherical fillers to minimize impact on viscosity, coupled with a polymer grafted canopy motif rather than short molecular ligands, is providing new approaches to improve processability. For example, recent work by Maillard et al.³⁸ suggests that the addition of grafted nanoparticles can in some cases increase the Young's modulus, the yield stress, and the strain to failure. What are the conditions under which these simultaneous improvements in properties can be achieved, and can this be realized on a practical scale is still under investigation. The additional design afforded by polymeric surface functionalization is also underlying approaches to spatially grade the nanoparticle interface to impart higher temperature thermo-oxidative resistance, such as bismaleimide

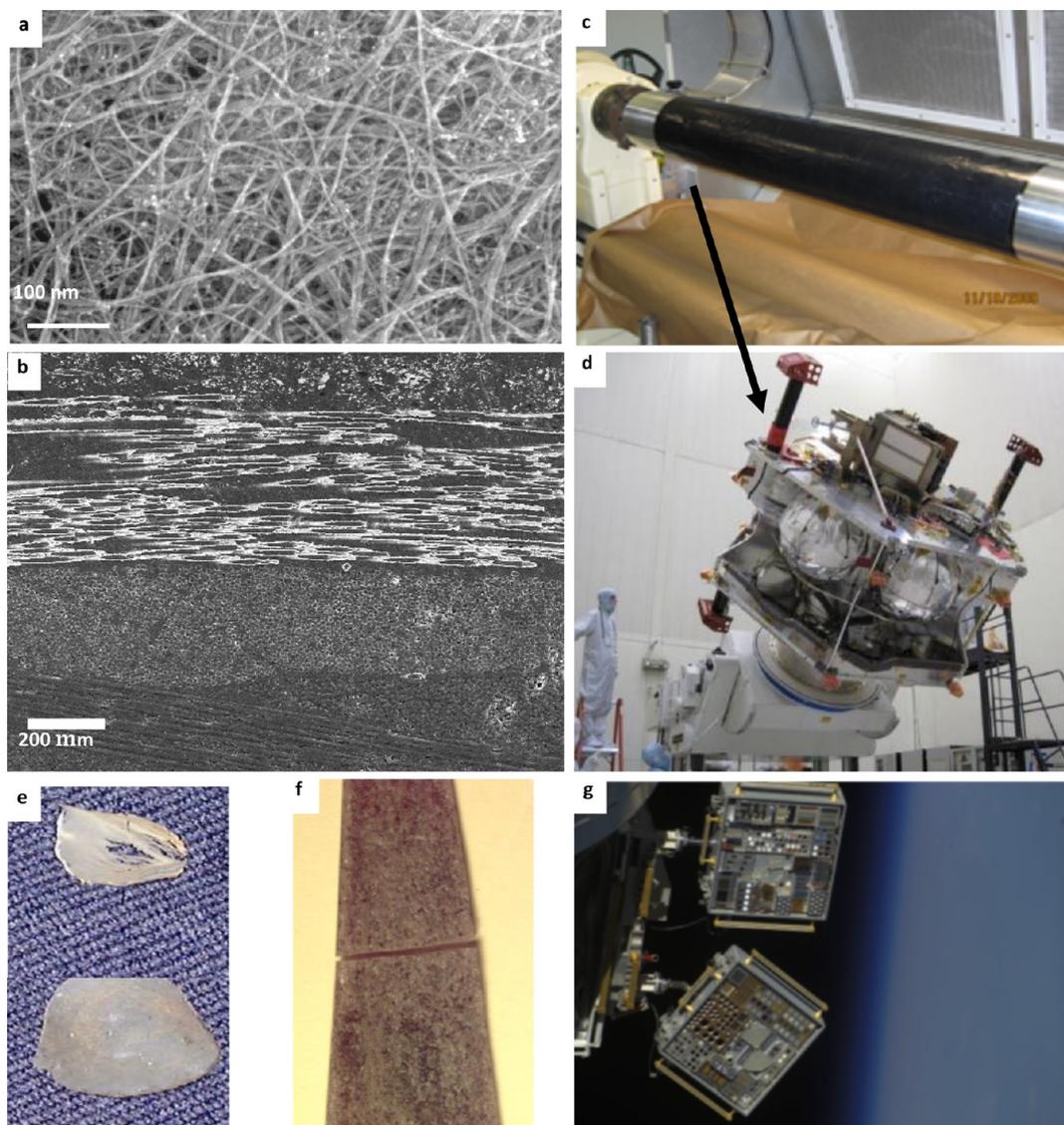


Figure 5. (a) Surface SEM of conductive nanoparticle veils (EMSHIELD, Nanocomp Technologies, Inc.) (unpublished, AFRL, courtesy Max Alexander). (b) Polished cross-section SEM of a conductive composite lay-up demonstrating integration of a resin-infused conductive nanoparticle veil (NiNanostrands, Conductive Composites) as a face sheet (top) on a composite structure containing metal-coated carbon fiber prepreg (middle) on top of the base composite layers (unpublished, AFRL, courtesy Max Alexander). (c, d) Lay-up of rocket engine motor support strut with CNT paper outer layer and location on main body of the Juno spacecraft (from ref 181). Examples of self-passivating character of PNCs (nylon-clay) when exposed to extreme environments, including (e) oxygen plasma (left, from ref 192) and (f) solid rocket motor firing (from ref 194). (g) Recent material survivability experiment on the space station (MISSIE 7), where the “suitcases” shown contain many different nanocomposite samples (courtesy of NASA).

or polyimide chemistries, or to incorporate reconfigurable cross-links to impart self-healing, shape memory, or mechanical adaptivity to the matrix.

Overall, three questions still limit the understanding of how nanofillers can best be used to enhance CFRC performance. First, how do we determine the optimal location, nanoparticle(s), and nanoscale morphology for a given composite design? Second, what is the cost-effective, CFRC-compatible processing approach to reproducibly achieve this nanoscale morphology? And third, what are the possible failure modes and associated signatures that limit lifetime? Fundamentally, the extent to which the properties of the matrix, most importantly its strength and toughness, can be enhanced by the synergism between the NP and the matrix is not adequately understood. Thus, without validated models for strength and a quantifica-

tion of the impact of structural variability (morphology, composition, etc.) on thermomechanical performance, PNCs will have limited integration into CFRCs design tools. The challenge is to untangle the inter-relationship between (a) the nonuniform stress/strain distribution in a heterogeneous nanosolid, (b) processing-induced gradients in local NP orientation, organization, and concentration, (c) impact of the NP on cure and property development of the local thermoset network, (d) residual stress arising from processing and cure within the heterogeneous structure, and (e) propagation of damage and energy release during thermomechanical loading. Crucial to this challenge, and to the validation of models, is the development of new characterization techniques that provide nanovoxel information about the NP-network interface as well as the application of analytics

on large data sets to quantify variability and the statistical nature of processing and failure initiation. Such tools are crucial for PNCs to impart additional multifunctionality to CRFCs.

Membranes for Gas Separations. The use of glassy polymeric membranes to selectively separate gas mixtures across a variety of applications, e.g., natural gas purification and carbon capture, is well established.^{195–198} Membrane separations are cost efficient relative to other current technologies and are characterized by an intrinsic trade-off between high flux and high product purity. The solution-diffusion mechanism governs transport behavior in glassy polymer membranes; i.e., the solute dissolves on the feed side membrane surface and then diffuses through to the product side. Thus, the flux of a gas is related to its permeability: $P_i = K_i D_i$, where K_i is the partition coefficient and D_i is the diffusion coefficient.^{199–203} Product purity is controlled by the selectivity, $\alpha_{ij} = P_i/P_j$. The inverse correlation empirically found between P_i and α_{ij} is frequently termed as the Robeson upper bound (Figure 6).^{200,203} Glassy polymer

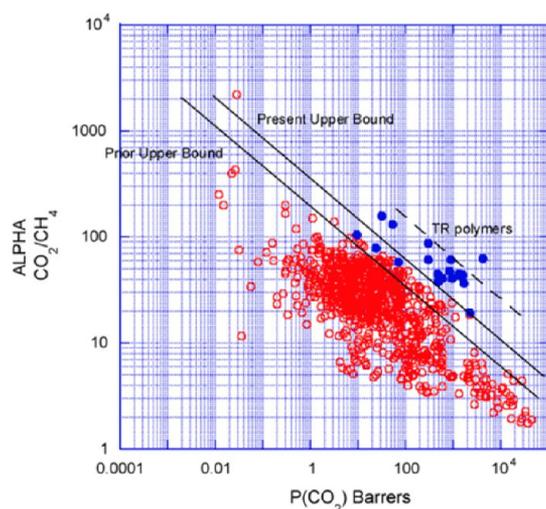


Figure 6. Relationship between the membrane permeability of CO₂ vs ideal CO₂/methane selectivity. The lines are “Robeson upper bounds”. Reproduced with permission from ref 200. Copyright 2008 Elsevier.

membranes are typically diffusion selective; that is, α_{ij} is controlled by the difference in D between the two species. The systematic manipulation of diffusion is therefore a key to improving separation membranes. A useful concept in this mode of molecular transport is free volume,²⁰⁴ a poorly defined metric that is attributed either to voids (due to imperfect polymer chain packing) or from chain dynamics and relaxation.^{205,206} Control over free volume is typically achieved through synthesis of new polymers with bulky side groups²⁰⁷ and/or stiff irregular backbones which frustrate local packing. However, these nonequilibrium glassy polymer-based structures spontaneously age, where the chains densify by improved packing as they approach their equilibrium states.

Pioneering work by Freeman has suggested that the addition of inert nanofillers can favorably modify the system free volume to achieve large increases in both permeability and reverse selectivities for butane/methane (Figure 7).²⁰⁸ This result, obtained from so-called “mixed matrix membranes”, is surprising in light of macroscopic ideas. In the case of transport behavior, macroscopic Maxwell ideas suggest that the addition of inert particles hinders molecular transport. Specifically, the permeability is predicted to decrease by a factor of $[(1 - \phi)/(1$

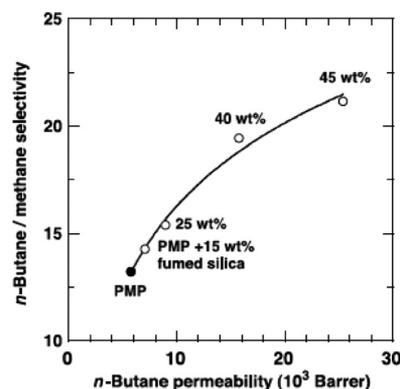


Figure 7. Ideal selectivity of *n*-butane to methane vs *n*-butane permeability for a P4MP membrane mixed with various loadings of silica NPs. Reproduced with permission from ref 208. Copyright 2002 AAAS.

+ $\phi/2$], where ϕ is the filler volume fraction, without affecting selectivity. The unexpected results of Freeman are understood in light of the unfavorable interactions between polymers and the inorganic filler, leading to dewetting and hence increased free volume. This poor compatibility causes the dispersion state, and hence membrane performance, to be intimately related to the detailed processing protocols.^{209,210} Thus, while improved performance results in a few cases, most situations conform more or less to the Maxwell ideas. The concept of controllably manipulating free volume in a temporally stable fashion by using nanoparticles in polymeric membranes remains open,^{207,211,212} and NP-based membranes have not yet found commercial application.

Progress in this field requires that we find sufficiently stable NP dispersions in polymer matrices that have controllable amounts of free volume. Achieving this goal in the framework of a glassy polymer matrix is particularly challenging because there can be both aging effects in the polymer matrix and temporally evolving NP dispersion states. Fundamentally, we do not fully understand what the free-volume concept embodies and how it can be manipulated by the addition of NPs. Is this a purely equilibrium concept, or do chain dynamics play a central role? What is the role of the NP in these situations, and what is the effect of the interface? Moreover, what is the interplay between polymer aging and NP diffusion? Priestley et al. reported that NPs can reduce aging even in glassy polymers.²¹³ In addition, we need to understand how the presence of NPs affect gas transport and also selectivity. Are any potential gains purely entropic in origin or can enthalpic effects (through the inclusion of specific functional groups) be used to optimize these separations?

Dielectrics for Electrical Insulation and Capacitors. High performance dielectrics are crucial to components that underlie modern society, ranging from gate dielectrics in transistors to high-voltage insulation and capacitors in power electronics. Polymer dielectrics afford a unique combination of processability with tailorability of resistance, permittivity, dielectric loss, DC dielectric breakdown strength, and gradual failure mechanisms.²¹⁴ For high voltage (HV) insulation, the use of inorganic fillers and coatings, e.g. boron nitride (BN), silica (SiO₂), alumina (Al₂O₃), titania (TiO₂), and silicon carbide (SiC), has been a staple for applications requiring higher temperatures and electrical stress, such as wire enamel, high voltage DC cabling, and insulation of motors, generators,

and transformers.²¹⁵ An optimized polymer–inorganic formulation not only improves electrical characteristics key to reliability and lifetime but also provides increased thermal conductivity, an adjustable thermal expansion coefficient, flame retardancy, and improved mechanical robustness. For instance, fillers are used to create anisotropic electrical properties that improve track (partial discharge) resistance of ground wall insulation of rotation machinery.²¹⁶ Inorganic filled high density polyethylene (XLPE) is used in extrahigh-voltage (EHV) DC cable between Spain and France. Layered architectures, such as Kraft paper, mica splitting, or platy fillers, are commonly used to increase reliability of insulation by impeding propagation of electrical breakdown trees.²¹⁷

For high voltage (HV) capacitors, electronic polarization within the dielectric affords ultrafast energy uptake and delivery.²¹⁴ Pulse discharge in the 10^{-3} – 10^{-6} s range is key to power-limited applications such as inverters in electric vehicles, defibrillators, power-conditioning equipment, high-frequency filtering, and pulsed-plasma thrusters. In contrast to HV insulation, film-based HV capacitors are conventionally unfilled, ultrahigh purity thermoplastics due to the challenges in reproducibly manufacturing large area, defect-free films from organic–inorganic blends within tolerances.

The key electrical characteristics for these high voltage dielectrics are the relative permittivity (ϵ_r), dissipation factor, and electrical breakdown strength (E_{BD}). For HV insulation, permittivity and dissipation factor are desired to be as low as possible, while for capacitors, the permittivity should be as high as possible while dissipation is minimized to provide maximize energy density, $U \sim \epsilon_0 \epsilon_r E_{BD}^2$ (for linear dielectrics) and discharge efficiency (i.e., fraction of stored energy recovered). Initial work by Nelson, Irwin, and others^{72,215} showed that replacing micrometer-sized particles with nanoparticles lead to numerous beneficial changes in polarization dynamics, including a lower loss tangent, mitigated space charge behavior, and an increased charge decay rate. Combined, these resulted in higher breakdown strength and longer mean time to failure. The relative micro- to nano-enhancements were attributed to a reduction in process-related defects, a refinement in the composite morphology, and an improved interface due to better filler–polymer interactions. Substantial fundamental and applied research has followed to establish a clear understanding of the influence of the nanoparticle size, shape, and composition on these key electrical characteristics. Similarly, the dispersion of the nanoparticles and the structure and composition of the particle–polymer interface are thought to play important roles.^{214,218}

The relative permittivity of a random heterogeneous material is classically described by nonlinear effective medium theories, such as the Maxwell–Garnett or Bruggeman models.^{214,219–221} These models indicate that the impact of high permittivity fillers distributed in a low permittivity matrix is less than predicted by a linear rule-of-mixtures due to local exclusion of the applied field from the particle into the matrix (e.g., Figure 8 summarizes the effective composite permittivity for nanocomposite films of uniformly dispersed polystyrene grafted titanium oxide nanoparticles). Although useful for initial assessment, these analytical models do not take into account internal charge distribution, charge trapping, or relaxation processes at the nanoparticle interface. Such processes may increase permittivity; however, saturation of local space charge distorts the internal field and may lead to premature failure. Shell models, such as those introduced by Tanaka^{222,223} and

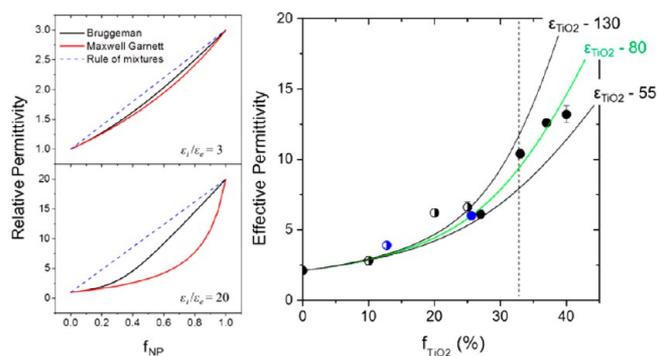


Figure 8. (left) Effective permittivity predicted from Bruggeman and Maxwell–Garnett mean-field theories for inclusions (ϵ_i) in matrices (ϵ_m) with dielectric constant ratio $\epsilon_i/\epsilon_e = 3$ (top) and $\epsilon_i/\epsilon_e = 20$ (bottom). (right) Composite permittivity (ϵ) versus volume fraction for various types of polystyrene grafted TiO_2 PGNs and correlation with the Bruggeman model for different estimates of ϵ_i for the nano- TiO_2 (unpublished, AFRL).

Lewis,²²⁴ provide a framework to understand such interfacial processes, their impact on charge transport mechanisms, and ultimately the frequency response of the permittivity and dissipation. Correlation between experiment and models though is quantitatively poor,^{214,218} pointing to the need for the continual codevelopment of theory and experiments to clarify the key factors underpinning the complex interplay between nanoscale morphology, field distribution, interface composition, relative Fermi levels, and charge polarization dynamics across a broad frequency range (DC–MHz).

In general, the addition of nanofillers and associated proliferation of internal interfaces substantially modify the distribution of the trapping sites within the dielectric. At intermediate carrier density, this affects the charge transport mechanisms and increases time to failure in HV insulation. For example, early work showed a 4-fold increase in partial discharge resistance for 10% silica added to polyimide.²²⁵ When coupled with percolation of the particle–polymer interface at high loadings (>10–20 vol %), these local polarization, charge relaxation, and trapping processes rapidly degrade the DC E_{BD} .²¹⁴ Therefore, the beneficial permittivity and interfacial charge trapping are limited to lower loadings depending on the specific electrical performance requirement of the HV nanodielectric insulation. On the other hand, for HV nanodielectric capacitors, one achieves at best a slightly improved ultimate energy density (U) for some polymer–nanoparticle systems at low loadings, but also a reduction in discharge efficiency. For example, recent work demonstrated that 5–10 vol % polystyrene grafted silica in polystyrene increases E_{BD} relative to the unfilled matrix, but PMMA grafted silica in PMMA with comparable morphology exhibits a precipitous decrease.^{226,227} Thus, nanoparticle dispersion alone is not the only critical factor, but just as critical is the relative Fermi level, and resulting interfacial band structure, for a given nanofiller–polymer system.

Numerous concepts have recently emerged to address these trade-offs, especially for HV nanodielectric capacitors. These include optimization of the dielectric character of the nanoparticle–polymer interfacial region and morphology engineering to homogenize local field concentration or impede charge transport. Examples include aligning anisotropic fillers^{227,228} to maximize effective permittivity in the direction of the applied field and adopting particles with graded

interfaces²²⁹ or core–shell architectures^{230–233} to mitigate local field concentration and deleterious dissipative mechanisms at the interface. For example, grafting the NPs with polymers rather than small ligands has been shown to reduce dielectric loss and improve storage efficiency.^{234–236} Also, polymer grafting sets a minimum particle–particle distance and hence diminishes the potential of agglomeration and formation of a critical hotspot that initiates internal failure within a HV capacitor.^{237,238} In other words, polymer grafting ensures that the critical flaw (i.e., very close particles) does not occur. This is especially important in nanocomposites containing high-permittivity nanoparticles, such as TiO₂ and BaTiO₃, where field exclusion from the nanoparticle results in substantial field concentration in the matrix near the nanoparticle surface in the direction of the applied field. Recent work has gone so far as designing the polymer grafts such that the polymer brushes of adjacent particles entangle, resulting in tough films, even without a matrix of free chains, with energy densities greater than the polymer matrix or blended nanocomposite. Finally, with regard to charge migration, interface architecture orthogonal to the applied field has been shown to hinder the electrical cascade in a film capacitor by dispersing energy over a larger volume analogous to motifs used for HV insulation. For example, the impact of layered architectures for HV capacitors was demonstrated in simulations²¹⁷ and experimentally in nanolaminates,²³⁹ layered-silicate nanocomposites,²⁴⁰ ordered block copolymers,²⁴¹ and microlayer coextrusion.²⁴²

In addition to morphology and interface, impurity concentration and process history have a substantial impact on initiation and propagation of dielectric breakdown. The necessary level of purity and attention to process history is seldom considered for nanocomposites. Extrinsic factors including absorbed water, entrapped gases, residual solvents, and ionic impurities dominate failure processes unless they are fastidiously removed.^{214,218} For example, as-received PMMA exhibits a DC E_{BD} for a film capacitor that is 50% lower than electronic grade PMMA that has been passed through a silica gel column and washed with methanol to remove impurities.²⁴³ With respect to processing, thermomechanical history and physical aging impact everything from chain alignment to the density and excess enthalpy of the amorphous regions. Driving the glass toward equilibrium not only increases density but also can increase DC E_{BD} for a film capacitor by 20–30%.²³⁵ The physics of how nanoparticles impact such polymer aging processes however is still not fully understood and thus have not been extensively considered in the high voltage performance of nanocomposites.

In general, PNCs for HV insulation are finding commercial application, but PNC for HV capacitors remains a challenge. Insulation with increased voltage stand-off uses nanoparticles to trap charge and create tortuosity orthogonal to the applied field. PNC dielectrics for HV capacitors and other power technologies, however, require a better understanding of dielectric failure within these nanoscale hybrid morphologies. For example, what are the relative roles of composition, morphology, and interface structure in local field distribution, carrier generation, and trapping at high fields across a broad frequency range (DC–MHz)? What is the role of physical and electrical aging on these polarization and transport mechanisms? How does electrostriction within these heterogeneous nanomorphologies impact failure? How sensitive are the optimal PNC designs to variability in morphology and interface functionalization? What scalable processing approaches are

available to avoid agglomeration and provide large area, defect-free films and coatings? As polymer systems with inherently high permittivity, such as PVDF, are combined with high permittivity nanofillers, how can the relatively high dielectric loss be minimized to reduce thermal contributions to failure and maximize energy storage efficiency?^{214,244} How can nonlinear nanoparticles and matrices be synergistically combined to avoid dielectric relaxation processes across requisite operation frequencies?²¹⁴ Are there novel characterization techniques to observe with statistical relevance failure processes to validate models? The promise of improving dielectric characteristics while optimizing the total property suite will continue to drive polymer nanocomposite dielectric research to meet the ever-growing demand for compact, highly efficient electric machines and power systems operating in more extreme environments, with multiple stressors, at greater intensity and higher repetition rates.

■ CONCLUSIONS

This Perspective has focused on the successes and the current limitations of polymer nanocomposites in four application areas. While filled networks are a commodity business that continues to need innovation, filled thermosets have a more niche market. The area of separation membranes is still in its infancy, but there is considerable promise, while the use of nanoparticles in the context of “nanodielectrics” is yet to come to fruition. While each of these topics has its own set of bottlenecks, an overarching concern in all of these cases remains the ability to control nanoparticle dispersion by designing NP/polymer interfaces, by adapting typical processing protocols, and by preventing morphology evolution during use. While some applications, such as rubber tires, have been able to address these challenges and achieve reproducible successes, it is apparent even here that considerable improvements remain to be exploited. We stress therefore that there remains considerable room for fundamental studies from new synthetic and processing strategies to predictions of macroscopic properties from first-principles or by inverse design. Moreover, when these studies are conducted within the context of specific applications, their findings will more rapidly impact the implementation of new and continually improving PNCs.

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Notes

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