

## **Chapter 11**

# **Industrial Applications Perspective of Nanodielectrics\***

**Enis Tuncer and Isidor Sauers**

Applied Superconductivity Group, Fusion Energy Division, Oak Ridge National Laboratory,  
Oak Ridge TN 37831-6122, USA

The field of nanodielectrics has had a significant impact on voltage endurance characteristics of electrical insulation. Improved time-to-breakdown behavior, resulting in reduced aging of insulation, and enhanced thermal stability are of considerable importance in industrial applications. This chapter discusses several specific aspects of nanodielectrics and their role in the future of electrical insulation and dielectric sciences.

### **Introduction**

One should not forget that power technology—high-voltage apparatus, transmission, and most electrical components—could not exist without satisfactory electrical insulation. It is a challenging task to design and optimize an electrical insulation system while energy demand, voltage levels, and operating temperatures are either increasing in conventional applications or decreasing to cryogenic temperatures in superconducting applications. In addition, these

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electrical components and equipment sizes are becoming smaller and more compact than conventional devices, placing greater demands on the insulation. New insulation materials are expected to have better endurance and to have better reliability than their conventional counterparts. Recent developments in composite materials filled with nanometer-size particles (defined here as particles in which at least one dimension is in the range 1–100 nm) have shown some interesting results, creating a new research field in electrical insulation being referred to as nanodielectrics (Lewis 1994; Lewis 2006; Nelson and Fothergill 2004; Cao et al. 2004).

A detailed description of dielectrics for high-voltage applications was provided in earlier work by Dakin (1978). In this chapter, our discussion will focus on recent developments in the field of nanodielectrics. Only solid insulation materials composed of nanoparticle-loaded polymers will be considered here. The chapter is organized as follows. Different aspects of the nanodielectrics will be considered starting with the background and challenges faced in synthesizing nanocomposites. Some of the significant advantages of the nanodielectrics and their impact on electrical insulation industry are then discussed in the context of dielectric breakdown and voltage endurance. Nanodielectric applications at high and low temperatures together with specific device/component applications are discussed as well.

## **Background**

Solid electrical insulation materials, or dielectrics, in high-voltage applications were made of natural materials, such as silk, glass, and ceramic materials in the early days of electrical power applications. However, improvements in materials science and the introduction of plastics have changed the perception that electrical insulation for different power components could benefit from new materials that were initially developed for or used in other technologies. Amazingly, there remain two areas where few advances have been

observed. Cellulose-based paper is still the main insulation material used in power transformers, and, in some sub-water cable applications, paper has been used for decades. Outdoor electrical insulation materials for high-voltage lines and bushings have been almost exclusively based on ceramic and glass technology; however, for the last several decades composite materials and polymeric materials with lighter and better surface performance than their earlier counterparts have been utilized.

The introduction of artificial rubbers followed by novel polymeric materials opened a new horizon in materials science and manufacturability after the World War II. Most of the hard-to-manufacture or shape materials used in different industrial applications were replaced by new plastics. In electrical applications, these plastics have been easier to shape and process compared to glass and ceramics. Most plastics/polymers without any filler particle inclusions do not possess sufficient mechanical strength; therefore, fillers have been introduced to improve the mechanical properties of polymers. Fillers like silica, asbestos fibers, alumina, titania, etc., have been extensively employed for property enhancement, and some of these fillers have also been used to improve the electrical properties of polymers.

It is still not completely understood how the dielectric breakdown in insulation materials occurs. However, it is known that degradation in materials, by heat or electric field, impurities, and/or defects, leads to undesired insulation failure. It is therefore critical that new methods of manufacturing defect-free or defect-tolerant materials be developed. It appears that nanoparticles in a nanodielectric help to create defect-tolerant regions. Improving properties of an existing material or synthesizing a new material has often been based on an Edisonian approach that requires testing many samples to build reliable statistics for a candidate material. Recent research results have illustrated that various nanodielectric systems have a promising future in electric insulation science.

## **Polymer nanocomposites**

Polymeric materials have been used by mankind for ages starting with natural materials (e.g. tar, shellac, etc.). Nowadays synthetic materials are produced in different forms for engineering applications. Although these synthetic polymeric materials can be employed without any fillers, they are often loaded with inorganic fillers either to reduce cost or to produce a product with unique properties that is suitable for multifunctional applications (Winey and Vaia 2007). The multifunctional features can be attributed to properties such as improved thermal/flame resistance (Xiong et al. 2007; Xie et al. 2002), moisture resistance, decreased permittivity (Nelson and Fothergill 2004; Tuncer et al. 2007), space-charge tolerance, increase mechanical strength, chemical resistance, and increased toughness (Koo 2006).

An example of improved thermal/flame resistance is hydrated alumina (aluminum trihydrate)-filled silicone rubber (Tuncer and Gubanski 2000), which is utilized in high-voltage outdoor insulation in transmission lines and bushings. The hydrated alumina used as a fire retardant in packaging applications and in high-voltage applications improves the arcing resistance of insulation. Another example is pure silicone rubber (polydimethylsiloxane—PDMS), which is brittle without any fillers, and is filled with either micrometer- or nanometer-size silica particles to improve the mechanical properties of the silicone (Koo 2006).

The nanocomposites concept started to appear in the late 1980s (Winey and Vaia 2007). These early works mainly focused on montmorillonite clays, material synthesis, and mechanical properties of the composites (Fukushima and Inagaki 1987; Usuki et al. 1993a; Usuki et al. 1995; Kojima et al. 1993a; Usuki et al. 1993b; Kojima et al. 1993b). Other metal oxides and metal fillers in the nanometer-size range in polymeric composites have also been investigated (Ciebien et al. 1998; Shi et al. 2004). The latter materials are used for electromagnetic shielding and flexible electrode structures (Kruisa et al. 1998; Althues et al. 2007).

Although the initial studies of nanocomposites focused on the improvements in the mechanical properties of the unfilled polymers, the benefit of using these new materials for thermal and electrical applications cannot be disregarded. The main advantage of using nanometer fillers is the large surface area they provide compared to the same volume fraction of micrometer fillers. The surface area highlights the importance of interfacial regions. For example there are many locations for the base polymer coils to form strong bonds to particle surfaces (Koo 2006). The increased surface area leads to an increase in the mechanical strength of base polymer. The effect of the increased interface area on electrical and optical properties was not clear due to the paucity of early investigations in this area. However, recent studies have shown that polarization in nanocomposites was made complicated because the measured dielectric permittivities of the base nanocomposite materials were lower than the permittivity value of the base polymer (Tuncer 2007; Nelson and Fothergill 2004). In addition the measured space charge densities, which are also related to the polarization, for nanocomposites were less than those of the base polymers (Nelson and Fothergill 2004). These unexpected observations reveal some of the unique application possibilities for polymer nanocomposite. While understanding the conduction and polarization mechanisms in dielectrics has been a major challenge for dielectricians since the beginning of the electrical era in the late 19th century, nanocomposite dielectrics have introduced new types of materials that need to be studied in addition to conventional dielectrics. Major areas of polymer nanocomposite applications are described in the following sections.

### **The commercial impact of enhanced electrical strength and endurance**

Solid dielectric insulation materials used in power applications mainly sustain the system voltage when used as a spacer. Any improvement in the dielectric strength of this spacer material would lead to thinner insulation for the same voltage level, leading to less electrical insulation material. According to Dakin (1978), “the

minimum insulation is often the least costly overall and provides the most compact equipment, but should not be achieved without assurance of adequate reliability.” In cases where the transportation cost and real estate values are important, less insulation would result in lighter systems and a smaller footprint than the conventional systems. Improvement in the dielectric strength would then lead to significant savings for manufacturers and utilities. Some specific examples of electrical components that can benefit from improved breakdown and endurance are power cables, transformers, and power capacitors.

In highly congested areas such as in large metropolitan cities, less insulation in power cables would result in more power delivery from the same conduit used for conventional cable applications. The space savings from the insulation cross section could be spent on conductor thickness, so larger currents could be carried on the same cable cross section. For short lengths (less than 2 km) a competing technology already exists, a cryogenic high-temperature superconductor power cable, which can carry approximately ten times the power in the same cross section. There are system-level issues for long cable lengths due to the current cryo-cooling technology. Polymeric nanocomposites have currently been studied as electrical insulation materials (Tuncer et al. 2007). This topic will be discussed later.

A similar argument on insulation thickness is true for the power transformers, such that less insulation would result in light and small power equipment. Once a better insulation material is found for transformers, a compact transformer can be installed on trailers for mobile applications in cases of emergency power recovery (Schwenterly et al. 2002; Schwenterly et al. 1999; Weber et al. 2005). In addition a compact transformer would be preferable in substation locations with high real estate values.

One should consider insulation design for power equipment and systems from the point of view of utility companies. For example, maintenance of the power grid and its components is an important part of the utility companies’ costs, improvements to which would

provide significant financial benefits. Improvements in the insulation endurance would lead to less maintenance and longer component lifetime compared to the conventional equipment built with conventional materials. It has been shown by Nelson and collaborators that polymeric composites with nano-size particles would have improved electrical properties (Roy et al. 2005, Nelson and Fothergill 2004). Although no significant enhancement in the dielectric breakdown strengths was observed, the studied materials indicated voltage endurance that was orders of magnitude longer than for the unfilled polymers or for composites filled with micron-size particles.

The voltage endurance, which is defined as the time to breakdown during electrical stress at a field lower than the field for immediate failure, would be clearly observed in electrical tree propagation. In nanocomposites that were studied, it was shown that the neat epoxy suffered breakdowns after 1 hr of tree initiation, while the epoxy nanocomposite survived for more than 5 hr (Alapati and Thomas 2008). The addition of nano-filler slowed down the electrical tree initiation and propagation. Similar studies on electrical and thermal properties of three component resin-based composites have been reported by Imai et al. in 2006 (also Imai et al. 2005). These systems contained nano- and micro-fillers in which the samples were made with nanometer-scale layered silicates and micrometer-scale silica fillers in an epoxy resin. The nanocomposites had a thermal expansion coefficient similar to that of the conventional filled epoxy. In voltage rising tests, the nanocomposite had 7% higher insulation breakdown strength than the conventional filled epoxy. In endurance tests under constant ac voltage (10 kV at 1 kHz), the nanocomposite had an insulation breakdown time of more than 20,000 minutes, whereas the conventional filled epoxy had a breakdown time of 830 minutes. Composite samples synthesized with epoxy resin and zinc oxide microparticles and nanoparticles had improved electrical treeing breakdown resistance (Ding and Varlow 2004). A small amount (<1 wt %) of nonlinear zinc oxide particles, which show non-ohmic conductivity as a function of electric field, was enough to increase the electrical tree resistance. Nano-structural differences created with the nanoparticles (also

nonlinear particles) show a clear indication of improvement in the insulation breakdown strength and endurance.

Indications of improved endurance can be attributed to less space charge buildup in insulation materials. Fothergill et al. (2004) reported results of dielectric spectroscopy and space charge measurements on epoxy resin filled with micro- and nano-sized particles. The particles in their study were titania ( $\text{TiO}_2$ ), alumina ( $\text{Al}_3\text{O}_2$ ), and zinc oxide ( $\text{ZnO}$ ). They concluded that the results did not indicate any significant effect of particle types and that the dielectric properties of such nano-filled composites are controlled by Stern-Gouy-Chapman layers ("interaction zones") around the particles (Lewis 1994; Lewis 2006).

The important implications regarding electrical insulation properties of metal oxide-filled nanocomposites were presented in a recent paper by Smith et al. (2008). It is now clear that polymer nanocomposites with nanoparticle fillers can exhibit improved dielectric breakdown strength and voltage endurance when compared to their neat resin or micrometer particle-filled counterparts. It has been stated that the inclusion of nanoparticles provides multiple scattering obstacles and trapping sites in the charge carriers' paths, effectively reducing carrier mobility and thus carrier energy. One can visualize the particles as holes and bumps on a landscape where a rolling ball would be deflected by bumps and are trapped by holes and argue that the structure of a disordered material (i.e., polymer or amorphous ceramics) would be similar. However, the landscape of a metal oxide nanocomposite is very different since the bumps and holes have the additional functionality of increased height and depth. This argument very well explains the experimental observation of high-electric-field properties of nanodielectrics. Such arguments were also mentioned in the view of homo-charge buildup at the electrodes, as determined by electroluminescence, pulsed electro acoustic analysis, and thermally stimulated current measurements in Smith et al. 2008.

Voltage endurance tests in the form of partial discharge (PD) experiments were carried out in epoxy nanocomposites where two



different particles were employed, nanoparticles of silicon carbide (SiC) and silicon dioxide (SiO<sub>2</sub>) (Tanaka et al. 2008a). It was observed that erosion caused by PD, as evidenced by the depth and eroded cross-sectional area, was much less in nanodielectric resin, where an increase in PD resistance was observed. In another study (Nakamura et al. 2008), enamel insulation materials on wires were investigated by also employing PD tests. Similar results, as reported by Tanaka et al. (2008a), were presented where a reduction of deterioration depth and of the surface condition of nanocomposite enamel wires were observed after repetitive surge voltage application with successive PD events/tests. It was clearly indicated that the erosion of nanocomposite enamel layers was suppressed in the depth of erosion caused by decomposition byproducts and dispersed in the longitudinal direction along the enamel surface, which contributed to the longer time-to-breakdown than for conventional wires (Nakamura et al. 2008). Resistance to PD was illustrated in epoxy nanocomposites and compared to neat epoxy resin and an epoxy resin with SiO<sub>2</sub> micro-filler (Kozako et al. 2005). In this work it was shown that the size of the particles is important and that smaller nanoparticles led to a more PD-resistant material compared to unfilled composites containing large particles.

Partial discharge resistance of nanocomposite resin with clays has been reported to be better than neat resin (Tanaka et al. 2008b). When samples with nano-micro clays were compared to the nanocomposite, they were found to be superior. A model based on a multi-core structure (described as interaction zones) was proposed to understand various properties of nanocomposites (Tanaka et al. 2005). The model was used to explain PD resistance of polyamide layered silicate nanocomposites.

A detailed study of PD degradation of polyamide both with and without nanoparticles was investigated by Kozako et al. (2004). Surface structure analysis showed that the roughness was considerably less in nanocomposites. The PD resistance of polyamide nanocomposites was significantly better than that of unfilled polyamide.

Huang et al. (2007a) presented a general review of polymer nanocomposites in which recent advances on polymer nanocomposites and investigations concerning the electrical conduction, dielectric strength, space charge, dielectric permittivity, dielectric loss, and PD were discussed.

Recent research indicates that engineered materials like polyhedral oligomeric silsesquioxane (POSS) would be useful in insulation applications. These materials contain extremely small silica particles (<5 nm) and are designed to be compatible with many thermosets and thermoplastics. A paper by Takala et al. (2008a) presents thermal, mechanical, and dielectric measurements conducted on polymer nanocomposites consisting of epoxy and POSS. Glass transition temperatures and tensile strength of the nanocomposites were lower than those of the neat resin. However ac and impulse breakdown strengths showed slight improvements with the addition of POSS. A similar investigation by the same group using polypropylene as the matrix also showed slight improvements in ac and impulse breakdown strength in nanocomposites with POSS (Takala et al. 2008b).

In most of the nanocomposite systems, particles are mixed in a matrix using an ex situ technique. Recent work by Tuncer et al. (2007) has focused on synthesizing particles in situ in the matrix. Fabricated polyvinyl alcohol titania nanodielectrics had breakdown strengths, measured in liquid nitrogen, that were significantly higher than those of unfilled polyvinyl alcohol. One can consider nanometer-sized particles as voltage stabilization additives.

Discussions related to particle-size-dependent properties were presented by Roy et al. (2005; 2007). Samples of polyethylene (Roy et al. 2005) and cross-linked polyethylene (Roy et al. 2007) with silica nanoparticles increased breakdown and voltage endurance. The endurance results were impressive, which indicated an increase in time scales of two orders of magnitude. This observation was attributed to the large interfacial region in the nanocomposites. These regions could be responsible for a reduction in charge

mobility and a change in the defect size (Roy et al. 2007).

In another polyethylene study (Huang et al. 2008), improvements in the physical properties of linear, low-density polyethylene/aluminum nanocomposites were reported with morphological properties. The frequency-dependent properties of the nanocomposites illustrated an increase in the dielectric constant of nanocomposites. It was found that highly filled nanocomposites had good mechanical properties and breakdown strength.

Direct-current transmission systems based on cables could benefit from the implementation of nanodielectrics. Reedy and Ramu (2008) reported on not only the electrical but also the thermal properties of nanocomposites. Previous investigations showed improvements in volume resistivity and the dc breakdown strength of nanocomposites. Nanocomposites of low-density polyethylene with magnesium oxide (MgO) nanoparticles showed a considerable improvement in their thermal properties as related to breakdown properties.

Other types of engineering polymers, polyarylene ether nitriles (PEN) and their corresponding nanocomposites, were studied with titania loading using sol-gel synthesis (Li et al. 2005). The dielectric and thermal properties of the films were characterized, and it was reported that mechanical and thermal properties were improved without dielectric breakdown degradation.

Outdoor insulation applications have also benefitted from nanocomposite dielectrics. For example, improved erosion resistance (electrical arcing tolerance), tensile strength, elongation at break, hardness, low dielectric permittivity, weather resistance, superhydrophobicity, and thermal stability are some of the material physical properties desired for outdoor insulation applications. Silicone rubber samples with nanometer and micrometer fillers have been studied and have shown that the fillers used were able to improve the erosion resistance of the rubber (Ramirez et al. 2009). The effect of surfactant on mechanical and erosion resistance was

also observed, indicating that excess surfactant had a negative effect on the considered properties.

Clays are nano-structured minerals with a huge potential for use as nanodielectric fillers due to their lower cost as compared to other engineered nano-powder. Clays can be used in various resins to improve the physical properties of the base materials; however, once nanoparticles are put in the base material, the curing procedure of the resin might change. Therefore, significant effort should be spent on the curing and mixing techniques. Tagami et al. (2008) presented the effects of curing agents and filler dispersion method on the dielectric properties of epoxy nanocomposites. They observed that, independent of the mixing methods, electrical properties (permittivity and conductivity) were more affected by the curing agents and less by the clay particles and the mixing method.

Increasing power electronics circuitry demands, due to inverters and converters, require that improvements in the packaging and electrical insulation materials be made. Okubo et al. (2007a and 2007b) and Hayakawa and Okubo (2008) investigated the breakdown lifetime characteristics under repetitive surge voltage application for nanocomposite-enameled wires. It was observed that the nanocomposite-enameled wires had a breakdown lifetime 1000 times longer than conventional enameled wires under surge voltage application.

### **Opportunities for enhanced high-temperature dielectrics**

High-temperature dielectrics are needed in generators (motors and drives), compact transformers, and specialty capacitors. In addition, the performance of insulation and its lifetime at various temperatures yield valuable information regarding its deterioration and the rate of deterioration (Berberich and Dakin 1956). As mentioned in the previous section, the dielectric breakdown and endurance of the insulation materials can be improved with nanoparticle addition in polymer insulation materials. Thermal integrity chemical effects such as oxidation, depolymerization, hydrolysis, undesired chemical

reactions, etc., and physical effects such as melting, softening, volatilization, hardening, cracking, and change in mechanical, thermal, and electrical properties should be considered (Berberich and Dakin 1956). These effects might be either postponed (slowed down) or avoided with the addition of nanoparticles.

Electrical insulation materials with better thermal properties can be used in electrical devices where large caloric power and improvements in heat dissipation are needed. An epoxy resin with high thermal conduction can be attained by reduced scattering of phonons, which affect the thermal properties, by controlling the nanoscale structure (Takezawa et al. 2003). Thermal properties and improvements were reported for two resins that were designed with liquid-crystalline molecules (mesogens), which act as inclusions in nanoscale. It was shown that thermal conductivities would become greater when the amounts of mesogens were increased (Takezawa et al. 2003); for example, a thermal conductivity increase of a factor of 5 could be attained compared to conventional resin.

Improvements in the thermal properties of a material can be achieved by addition of carbon nanofibers or nanotubes (Frommann et al. 2008). When high shear mixing was used to disperse and distribute the nanofibers, a good dispersion of the fibers within the polypropylene matrix was observed. Thermal property analysis showed thermal stability enhancements and an increase in the melting temperature of polypropylene. The fibers also increased the storage modulus and decreased the mechanical loss factor ( $\tan\delta$ ). The main advantage of using fibers was the improvement in the thermal conductivity.

Polyimides are high-performance polymers with good electrical insulation properties. Polyimide samples prepared with silica nanoparticles showed that the thermal stability via thermogravimetric analysis (TGA) was improved with nanoparticles (Zhang et al. 2007). Aluminum nitride-filled nanocomposite polyimide was characterized as a dielectric material in microelectronic packaging (Saeed et al. 2006). The mechanical

properties, elastic modulus and strength, were improved with an increase in filler content.

Studies of the electrical properties of polyimide, characterized by the thermally stimulated depolarization method, have concluded that the nature of conductivity of this material is ionic (Cao and Irwin 2003). Nanometer-size particle inclusions altered the main thermally stimulated current peak to higher temperatures, which indicated that nano-fillers changed the trap density and depth. Cao and Irwin (2003) concluded that nanocomposite polyimide would not degrade its electrical breakdown strength.

A different approach to investigating polyimide nanocomposites was performed by Jiaqi et al. (2006). Electroluminescence experiments on unfilled and nanoparticle-filled polyimide films were conducted under dc field. Pre-breakdown fields for filled polyimide were higher than those for the unfilled material, which also indicated improvements in the dielectric breakdown characteristics of polymers with nanoparticle addition. A polyimide mixture with varied amounts of alumina has shown improved thermal stability from TGA and electrical aging performance as compared with pure polyimide film (Hong et al. 2006a).

A detailed analysis of electrical properties of polyimide nanocomposites as insulation for enameled wires and investigations of surface erosion under stress and partial discharge resistance showed that nano-filled polyimide have improved insulating properties (Saeed et al. 2006).

Anisotropic silicates were proposed to enhance the physical properties of polyimides (An et al. 2008). Rod-shaped silicates were mixed into polyimide, which resulted in significant improvements in strength and toughness as well as increases in the thermal decomposition temperature.

Various insulating varnish nanocomposite systems composed of polyester and low loading of nanoparticles of fumed silica, silica and titanium dioxide, zinc oxide, or clays (montmorillonite) were

processed, and their mechanical, electrical, barrier, and thermal properties were investigated (Gornicka et al. 2007). The polyester varnishes are utilized in high temperature insulation applications. Therefore, improvements in their dielectric properties (electrical strength, resistance to pulse voltage) would be possible by incorporation of various nanoparticles. The inclusion of nanofillers has also exhibited an increase in thermal endurance (Gornicka et al. 2007).

### **Cryogenic applications and other extreme environments**

Electrical insulation material requirements for technologies such as cryogenic (high-temperature superconductive) power applications (Schneider 1991; Dale et al. 1990a; Dale et al 1990b), novel energy applications such as fusion (Moreschi et al. 2003), and space devices (Masayuki 2004) have been more demanding than the conventional insulation applications due to a lack of interest in these applications in the past. However, for the last several decades, improvements in superconducting materials and industrial processing techniques have made it possible to manufacture devices with superconductors. Early applications were low-voltage superconducting magnets, which could tolerate imperfections in the insulation (Forsyth 1993) since the voltage stresses were low. In cryogenic applications, insulation failure could be caused by mechanical stress as well as a mismatch of thermal properties of components or the intrinsic thermal properties of materials. In addition the entire insulation system needs to be designed to be PD free due to the likelihood of electrical degradation (Gerhold 1998; Gerhold 2002; Gerhold and Tanaka 1998; James and Sauers 2004; Sauers et al. 2004), leading to insulation failure. Many micro-filler composite materials have been characterized for cryogenic insulation applications (Sauers et al. 2004 Tuncer et al. 2007a). However the addition of micrometer-size particles has generally lowered the dielectric breakdown strength of base polymers. Not as much research is being conducted in nanodielectrics for cryogenic applications as is being done for conventional ones.

Recent studies on nanocomposite dielectrics have illustrated that nanofillers could be used to improve mechanical and thermal properties without degrading dielectric properties. Several nanocomposite systems characterized by the authors of this chapter have demonstrated the potential of nanodielectrics in cryogenic applications. The materials selected for cryogenics applications were either based on thermoplastics—polyvinyl alcohol (Tuncer et al. 2007b; Tuncer et al. 2008) or polymethyl methacrylate (Tuncer et al. 2009)—or a thermoset—Araldite® 5808, from Huntsman Advance Materials, Inc. (Tuncer et al. 2007a). It was shown that nanometer-size particles could serve as a voltage stabilizing additive (Tuncer et al. 2008).

Field grading and tailoring the permittivity are important in cryogenic applications, with possibilities of adjusting permittivity using barium titanate nanoparticles. These materials have been demonstrated to be potential candidates for cryogenic capacitors or for field grading applications (Tuncer et al. 2008). Monodispersed cobalt ferrite nanoparticles have improved the dielectric characteristics of polymethyl methacrylate (Tuncer et al. 2009). The structural and dielectric properties of nanocomposite dielectrics were presented with plausible explanations for the observed low effective dielectric permittivity values in nanodielectric systems. Nanoparticle composites with large permittivity particles would have a low dielectric permittivity regardless of what the permittivities of the nanoparticles are when the particles are coordinated with a low dielectric permittivity surfactant (Tuncer et al. 2009). Systems with low permittivity surfactants demonstrate better electric potential distribution in material that improves the electric stress distribution and breakdown strength (Tuncer et al. 2009).

Glass fiber composites, such as FR4, G10 or G11, are often used as structural support in fusion, space, or power applications. Recent studies on the dielectric and mechanical properties of nanowire-alumina-filled polybutylene terephthalate/glass-fiber composites have been investigated (Yu et al. 2006). A crack bridging toughening mechanism was observed in which nanowires reduced



the crystallinity. It was concluded that alumina wires may have reduced the number of micro-defects and thus improved the electrical strength of the nanocomposite system.

### **High-voltage stress grading materials and conducting nanocomposites**

Different fillers are incorporated into polymers to improve their electrical characteristics. For example zinc oxide and silicon carbide particles have been used to achieve nonlinear field dependence (Donnelly and Varlow 2003; Strumpler et al. 1995; Mårtensson and Gäfvert 2004) so that the composite materials could be used in locations where high electric fields were anticipated. Recent research has shown that the micrometer-size particles can be substituted with nanometer counterparts. For example, Hong et al. (2005) showed that zinc oxide/low-density-polyethylene nanocomposites have a lower percolation threshold and a decrease in resistivity with filler concentration compared to the microparticle-filled conventional composite. They also observed that the dielectric breakdown strength was higher for the nanocomposite.

Designing conductivity of materials is of importance for dc power and resistive field grading applications. An increase in permittivity could be expected in nanotube-filled polymers due to Maxwell-Wagner-Sillars polarization below the percolation threshold. However, the percolation threshold is highly dependent on the shape and dimension of the tubes. Experimental and numerical simulation results on nanotube-polymer-composite systems have been presented by various researchers who took into account percolation and charge transport aspects of the systems (Simoes et al. 2009; Jiang et al. 2007).

Experimental studies on nano cadmium sulfide polyvinyl alcohol illustrated a high electronic conductivity, which linearly followed particle concentration. The results have shown that the cadmium sulfide nanocomposites could be implemented for antistatic charge dissipation and electromagnetic shield applications.

Percolation threshold, dc conductivity, and dielectric strength of polyethylene aluminum nanocomposites were investigated to better understand the physics of nanocomposites. Huang et al. (2007b) investigated physical properties of nanocomposites with the percolation theory. They reported various percolation thresholds for the physical properties; the dielectric breakdown had the lowest of all.

Anisotropic composites could be used to design improved electrical response. In a recent study employing dielectrophoresis, anisotropic barium titanate silicone composites were created (Tomer and Randall 2008). The electrical properties of these composites were found to be dependent on the anisotropy present in the system. Materials with tailored structure/anisotropy could be employed to control dielectric breakdown strengths and nonlinear conduction.

A power law behavior in electrical properties as a function of filler content was observed near the percolation threshold for styrene-acrylonitrile graphite sheet composites (Panwar and Mehra 2008). A similar study with polystyrene/foiled graphite has illustrated that a nonlinear-to-linear dependence in current-voltage characteristics of the composites was observed as the volume fraction of graphite was increased over the percolation threshold (insulator-conductor transition) (Srivastava and Mehra 2008).

Contact resistance lowering applications require easy-to-apply conducting grease. Benedetto et al. (2007) have designed a nanocomposite material with lubricant and improved electrical properties. The material was based on carbon nanotubes and different electrochemically grafted organic matrices.

### **Applications in the capacitor industry**

Insulating materials with high permittivity and high breakdown strength would yield large electrical energy density. The stored

energy  $W$  is expressed as a function of the dielectric permittivity  $\epsilon$  and the square of the applied electric field  $E$ <sup>1</sup>,  $W=1/2\epsilon E^2$ . It would be beneficial to improve the design field, where, for example, an improvement in twice the design field would quadruple the stored energy. However this is not an easy task. It is usually more straightforward to increase the dielectric permittivity of a composite just by increasing the content of the high permittivity component. Recent results and developments in nanocomposite polymers have illustrated that an increase in permittivity has also yielded either improvement or no significant change in the dielectric breakdown strength (which is related to the design field). Li et al. (2007) have discussed several issues in nanocomposite dielectrics by analyzing the effective permittivity, breakdown strength, and electric energy density of systems with an effective medium approach. They have concluded that the structure of nanocomposites would play an important role, and special attention should be given to control it.

The synthesis and properties of ferroelectric nanometer-sized powders play an important role in the fabrication of nanocomposite materials for capacitor applications. Lu et al. (2004) discussed the structural and physical properties of inorganic materials in the context of their particle size. A detailed description was given on the characteristic parameters of capacitors with enhanced dielectric permittivity, breakdown voltage, ageing resistivity, mechanical strength, etc. When these particles are introduced to polymers, the physical properties of composite systems could be tailored to achieve the best performance (Tan et al. 2006).

Porous materials composed of carbon nanotubes and doped polypyrrole showed high specific capacitance of 131 F/g when the mixture is 50-50 (Oh et al. 2008). These new nanocomposite materials could be used in capacitors and electrodes for batteries and electromechanical actuators.

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<sup>1</sup> It is particularly important that the breakdown strength be presented or considered such that a capacitor device operates at the designed voltage level.

Poly(vinylidene fluoride) (PVDF) is a high-permittivity polymer proposed for use in capacitor applications. A nanocomposite based on PVDF and poly(p-chloromethyl styrene) coated copper phthalocyanine (CuPc) oligomer has been shown to have a dielectric constant of 325 at 100 Hz for the composite with 15 wt % filler particles (this value is approximately 7 times larger than PVDF with CuPc particles, and about 40-fold higher than unfilled PVDF) (Wang et al. 2009).

Surface-modified barium titanate nanoparticles in poly(vinylidene fluoride-co-hexafluoropropylene) have been shown to possess large relative permittivities and unusually high dielectric breakdown strengths (Kim et al. 2007a).

High-performance polymers and high-permittivity ceramics have been studied for capacitor applications. One such composite system is barium titanate-filled polyimide nanocomposites. Dang et al. (2008) have reported a high dielectric permittivity (20), high breakdown strength (67 kV/mm), and high thermally stable nanocomposite systems.

Li et al. (2005) have studied nickel and barium titanate nanoparticle-filled polyamide systems where both systems yielded high relative permittivity for embedded capacitor applications.

Cryogenic capacitors would be needed if cryogenic power applications were built with the same coolant system or in space applications. Tuncer et al. (2008) reported electrical properties of a nanocomposite system composed of polyvinyl alcohol and barium titanate nanoparticles that could be used in a cryogenic capacitor. The sample with the highest filler concentration had a relative permittivity approximately equal to 9 and 1% breakdown probability breakdown strength at 20 kV/mm.

A nanocomposite system with conductive polyaniline nanofibers dispersed in polyvinylidene fluoride-trifluoroethylene copolymers exhibited a dielectric constant 50 times higher than that of the ferroelectric polymer matrix (Wang et al. 2008). The drastic

reduction in electric field strength that was required to switch spontaneous polarization of the matrix was attributed to the nanofibers.

### **Multi-functional opportunities**

Actuator materials capable of converting mechanical energy to electrical energy or electrical energy to mechanical energy are needed for many industrial applications, such as robotics, micro air vehicles, flat loudspeakers, micro-electromechanical systems, and microfluidic devices. In actuator applications large displacement with high precision and speed are required with durability and reliability. The elastic energy related to the mechanical properties of the actuator is the product of half of its Young's modulus  $Y$  and the strain  $S$ ,  $W_a = 1/2YS^2$ . This energy is supplied with the electrical energy (Maxwell stress tensor), which is  $1/2\epsilon E^2$ . Hence, for the highest strain (displacement), a material with low stiffness (low Young's modulus), high breakdown strength, and high permittivity is desired. With recent developments in nanocomposites, novel materials for actuators could be tailored because of the potential to increase permittivity and keep dielectric strength appreciably high. In actuator applications, the electrode materials are considered to have low stiffness.

Polyurethane with a conductive filler nanocomposite system was proposed, and among the fillers that were considered (carbon black, vapor grown carbon fiber, and silver powder), carbon nanocomposite electrode had the largest displacement (Kim et al. 2007b).

An ionic polymer metal composite and a nanoclay-filled polymer nanocomposite were studied for actuator applications (Paquette et al. 2003). It was shown that the current/voltage ( $I/V$ ) curves could be used to create an optimized effective polymer actuator. An approach similar to that of Paquette et al. (2003) was proposed by employing nafion<sup>TM</sup> and carbon nanotubes (Lee et al. 2006). It was concluded

that nanocomposites produced a significantly larger elastic modulus and improved electromechanical coupling compared to those of the unfilled nafion<sup>TM</sup>. Uniform distribution of nanotubes is needed for improved performance (Lee et al. 2004).

A polyurethane polymer with little volume fraction of copper phthalocyanine oligomer nanocomposite exhibited a colossal dielectric (relative permittivity around 10000) and electromechanical response (Huang et al. 2005).

A piezoelectric paint was investigated with nanowires (instead of nanoparticles) of barium titanate (Feenstra and Sodano 2008). The employed nanowires improved the electromechanical coupling threefold compared to the nanocomposite.

## **Conclusions**

An overview of polymeric nanocomposites and their potential use in industrial applications is provided in this chapter. It is clear that continued developments in chemistry and materials sciences are critical to electrical insulation research in the field of nanodielectrics.

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