

Materials and Applications of Polymer Films for Power Capacitors with Special Respect to Nanocomposites

Maximilian Streibl and Roman Karmazin

Siemens AG
CT REE MDM FMP-DE
Otto-Hahn-Ring 6, 81739 Munich, Germany

Ralf Moos

University of Bayreuth
Department of Functional Materials
Universitätsstraße 30, 95440 Bayreuth, Germany

ABSTRACT

This review highlights the research conducted on polymers, especially on polymer nanocomposites for electrical energy storage applications in power capacitors. State-of-the-art neat polymers are addressed as well as blends of polymers. Special emphasis is given to polymers filled with ceramic nanoparticles – polymer nanocomposites. The aim of this contribution is to overview the different approaches being made to improve the properties of dielectric polymer films for power capacitors. It concludes with an outlook on the research topics that should be addressed in the future.

Index Terms — dielectric polymer nanocomposites, nanodielectrics, polymers, dielectric performance, multi-core model

1 INTRODUCTION

THE growing demand for environmentally friendly technologies requires a rapid development of possibilities to gain energy from renewable sources. Above all, offshore wind platforms are subjected to unprecedented growth of interest. Since being located several hundred kilometers from shore, energy transfer for long distances is challenging as well as energy storage for long periods. Out of all the different storage devices, only capacitors meet the main requirements for the application within off-shore platforms, which are high energy density due to limited space on platforms and high reliability [1]. High power capacitors play an important role in those tasks. A comparison of different types of capacitors is given in figure 1. Depending on the type of dielectric material, a capacitor may be suited for high voltage or high capacity applications. Ceramic and electrolyte capacitors are mainly used in power electronic applications due to their relatively high voltage and high capacitance respectively. Among different types of capacitors, the ones with polymer films as dielectric materials are preferably used nowadays on off-shore platforms. Polymer film based capacitors exhibit excellent self-healing behavior and low cost [2]. Different polymer film materials used in capacitors are listed in table 1. T_{\max} describes the maximum operating temperature that can result from different properties of the polymer. This may be a significant

drop in BDS due to exceeding crystallization temperatures (T_{cr}) in the case of semi-crystalline polymers or the glass transition temperature (T_g) for amorphous polymers. State-of-the-art capacitors are based on polypropylene (PP) films [2].

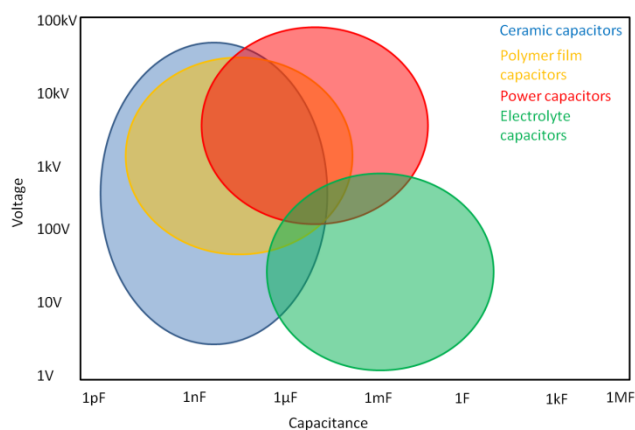


Figure 1. Comparison of different capacitor types with regard to voltage and capacitance. Data collected from [1–4].

Although it has a low permittivity, the high breakdown field strength (BDS) and low dielectric loss make BOPP (Biaxially Oriented Polypropylene) the ideal material for high energy density applications. Even though polyesters, like PET, can store more energy per volume, their higher dissipation factors lead to extended heat production that prohibits the use in off-shore platforms [2]. Increasing both permittivity and breakdown field strength, i.e., increasing energy density

without increasing power losses, are the key to improve capacitors further. Polymer blends and composite materials offer a good possibility to achieve this target. Especially, the group of nanocomposites has attracted recent attention in that respect [5]. An unusual electrical behavior is due to interfacial effects between filler nanoparticles and the polymer matrix. Such an interface has a large surface area and dominates the properties of the composite materials on the macroscale [5]. The following review sketches the development of polymer films from neat polymers over polymer blends to polymer nanocomposites with respect to their application in the field of power capacitors. Special attention is paid to nanocomposite materials. The different theories of functionality of nanocomposites will be explained and experimental work that has been conducted over the past 10 years will be summarized and compared with theoretical approaches. A path for the further development of power capacitors based on nanocomposites will be evaluated as well.

Table 1. Properties of different polymer films for capacitors [2, 3, 6–14]. For the abbreviations, see caption of Figure 2. ϵ_r : permittivity, T_{\max} : maximum operating temperature, BDS: dc breakdown strength (at RT (room temperature)), $\tan(\delta)$: dielectric loss factor (at room temperature, 1 kHz), w_{el} : electrical energy density of the capacitor, * @ 1 kHz & RT, + 100 Hz & RT, ^a ball-plane electrode, ^b metalized Al-electrodes on both sample sides with 35 mm electrode diameter, ^c metalized electrode with 2.5 mm diameter, ^d plate-plate electrodes with 2 cm² electrodes, ^e plate-plate electrodes with 1.26 cm² electrodes, ^f metalized electrodes with 0.25 mm² electrodes, ^g cylinder-plate-electrodes, ^{na} no data available.

Polymer film	ϵ_r	$T_{\max} /$ °C	BDS / V/ μ m	$\tan(\delta) /$ 10^{-2}	$w_{el} /$ J/cm ³
BOPP	2.2*	105	820 ^a	<0.02	1-1.2
PE	2.2*	<80	290 ^b	<0.02	-
PET	3.3 ^{na}	125	570 ^{na}	<0.5	1-1.5
Solvent cast PC	3.1 ⁺	125	<820 ^a	<0.15	0.5-1
PVDF	12 ^{na}	125	590 ^{na}	<1.8	2.4
PEN	3.2 ^{na}	125	550 ^{na}	<0.15	1-1.5
PPS	3.0 ^{na}	200	550 ^{na}	<0.03	1-1.5
PVDF-CTFE	11. ⁺	125	750 ^c	5	27
P(TFE-co-VDF)	10.2 ⁺	270	>225 ^c	3	2
PI	3-7 ⁺	200	>600 ^{na}	1-4	1.8-2.8
PEEK	3.2 ^{na}	150	400 ^d	0.4	-
Siloxane	8.6 ^{na}	150	-	6	-
PEI	3.2 ⁺	200	>550 ^a	0.2	-
PTFE	2.1 ^{na}	260	650 ^c	0.05	-
FPE	3.3 ^{na}	270	-	0.26	-
PMMA	4.0 ^{na}	-	245	5	-
Epoxy	3.5 ⁺	<90	120	5	-

2 POLYMERS AND POLYMER BLENDS FOR POWER CAPACITORS

Although biaxially oriented polypropylene (BOPP) remains state-of-the-art for application in power capacitors, its temperature limitations speed up the development of high-temperature dielectric polymer films. Alternative polymers and polymer blends, their dielectric properties and application possibilities in power capacitors are discussed in this section.

2.1 NEAT POLYMERS

The dielectric properties of various polymers are reviewed and summarized by Tan *et al* [3]. Results are given in Figure 2. Obviously, polymers with the highest dielectric strengths also exhibit low losses but low permittivities as well. As already noted, BOPP is state-of-the-art in the area of power capacitors. Films with excellent dielectric properties are fabricated by stretching cast PP films in both longitudinal and transverse machine directions. Such a stretching increases the orientation of PP, thus allowing the breakdown field strength of the films to increase about twofold when compared to non-stretched PP of similar thickness. It was shown that BDS increases with higher biaxial stretch ratios due to increased orientation – spherulites are converted to fibrillary networks of lamellar crystallites oriented in the film plane. It was also found that certain crystalline morphologies (initial β -phase content in the cast film above a certain value) may induce microvoids and lead to porosity formation after biaxial stretching. Since the base resin influences the morphology of the film, molecular weight, purity, etc. of the base resin also ultimately influence breakdown performance of the finished capacitor [15].

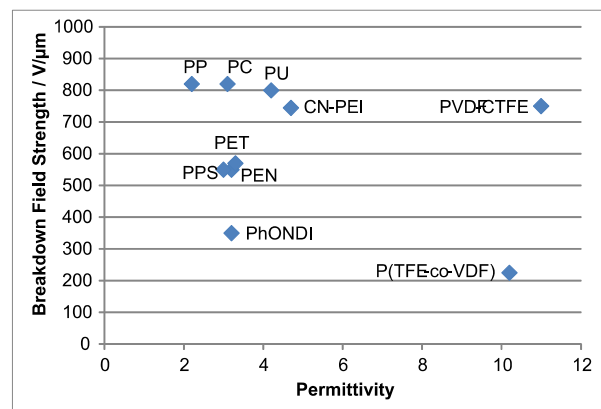


Figure 2. Dielectric strength and permittivity of polymers: With data for polypropylene (PP), polycarbonate (PC), cyano-modified polyetherimide (PEI), N-phenyl-7-oxanorborene-5,6-dicarboximide (PhONDI), polyurea (PU), polyvinylidene-fluoride-chlorotrifluoroethylene (PVDF-CTFE), and poly(tetrafluoroethylene-co-vinylidene fluoride) (P(TFE-co-VDF)) collected from [3] and data for polyethylene terephthalate (PET), poly(p-phenylene sulfide) (PPS), and polyethylene naphthalate (PEN) collected from [2].

Laihonen *et al* [16] evaluated the breakdown field strength of different polypropylene films with different electrode areas. It was found that the BDS decreases with increased electrode areas. This can be explained with the Weibull area scaling law. Additionally it was found that there seem to be two breakdown populations: some (1 – 15 %) of all breakdowns appear at low field below 400 V/ μ m, the high field failures with a different slope in the Weibull plot were found above 400 V/ μ m. Electrode effects are assumed as the main explanation for the low field breakdowns but weak spots in the film are considered to play a significant role, too. This was confirmed for a lower quality film prepared from the same base resin as other samples in the study that showed relatively poor performance due to weak spots. The main parameter

besides the base resin quality (e.g. chemical purity, isotacticity, etc.) affecting the high field breakdowns is the roughness of the film. Increasing the film roughness decreases the BDS. However, it was not possible to predict breakdown field strength of power capacitors based on Weibull analysis. Processing of polymer films to form capacitors affects the overall breakdown field strength. The BDS can be improved by optimized processing of the film to build capacitors (e.g. winding, metallization and impregnation) as less weak spots are generated. However, incorrect processing may introduce new weak spots into the film, which negatively influence the insulation properties of PP, especially at low fields which entails lower capacitor performance [16].

A high energy density capacitor was introduced by Slenes et al. [17]. Kraft paper was impregnated with a dielectric polymer, serving as a siloxane backbone with two polar groups to increase the permittivity to $\epsilon_r' = 9.3$. The loss factor was 0.03. Impregnated paper was processed in order to be compatible with polymer film capacitor processing. Thus, a wound roll of paper with evaporated electrode was prepared and characterized in oil to improve the insulation of the capacitor. The achieved energy density was 2-3 J/cm³ at voltages above 3 kV tested on capacitors in the range of 6 to 12 μ F.

Zhang et al. suggested polymethylpentene (PMP) as an appropriate replacement material for BOPP [18]. PMP is a lightweight material with the same dielectric constant, exhibiting lower losses and better high temperature resistance than BOPP. The operation temperature of PMP is as high as 230°C. High voltage performance of PMP can provide faster discharge, higher power density, lower heat generation and temperature rise and higher operation temperature than BOPP capacitors [18].

Generally, the high temperature polymers are in the focus of development, since the BOPP has a relatively low maximum operating temperature of only about 105 °C [2]. This maximum operating temperature can only be achieved with high purity base resin that has been optimized over the last years. An overview of high temperature polymer capacitor films is provided by Tan et al. [3]. The important properties of common high temperature polymers are summarized in Figure 3. A relatively big group of polymer films exists, such as polyethyleneterephthalate, polycarbonate, and others, with an operating temperature in the range of 100 °C to 200 °C [6].

Polyvinylidene fluoride-chlorotrifluoroethylene (PVDF-CTFE) is known for its high permittivity and high BDS of over 500V/ μ m. However, its high losses and its comparably low working temperatures render it unsuitable for a wide spectrum of electronic applications. Furthermore, the high price and processing issues limit the applicability of PVDF-CTFE as a neat dielectric polymer. Better known are polymer-ceramic composites with PVDF-CTFE [19]. This polymer is mainly applied as a hydrophobic membrane material for battery separators [20, 21].

Polyetheretherketone (PEEK) exhibits a low thermal stability of its dielectric properties. Its losses increase

dramatically over 140°C [4]. Its permittivity is slightly higher compared to PP, $\epsilon_r' = 4$ [22]. PEEK is available as an amorphous or a semi-crystalline material. Ho et al. evaluated the influence of crystallinity on the electric resistivity and breakdown field strength at elevated temperatures of 140°C [9]. The electric resistivity of the amorphous phase was found to be lower than the one of semi-crystalline material at electrical fields below 100 MV/m. Measurements above 100 MV/m were not possible since samples broke down. This was accentuated by prolonged aging at elevated electric fields to which the samples were subjected at 140 °C.

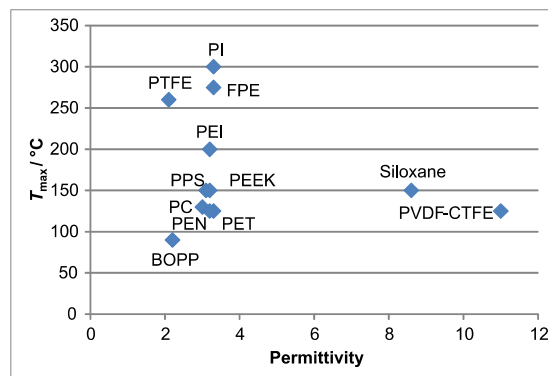


Figure 3. Maximum operating temperature and permittivity of dielectric polymers. Data collected from [2, 3].

Only a few neat polymers can be used at temperatures over 200 °C. Polyimides (PI) are a group of polymers with excellent mechanical properties, superior thermal stability, low dielectric losses in the range of 1 % to 4 % [6, 23] and BDS higher than 600 V/ μ m [7]. These properties make polyimides well suited for application in power capacitors, but they are very expensive. The permittivity is typically in the range of 3-5 [6]. Different polyimides with bipyridine groups were synthesized [6] to increase the dielectric constant of pure PI. A novel diamine, (5,5'-bis [(4-amino) phenoxy]-2,2' bipyridine) was polymerized by different dianhydrides. The synthesized polyimides exhibit excellent properties making them candidates for power capacitor application: $\epsilon_r' = 5.5-7.2$, $\tan(\delta) < 0.04$; energy densities of $w_{el} = 1.81-2.77$ J/cm³; melting temperatures between 275 and 320 °C, and a tensile strength of $\sigma_B = 175-221$ MPa [6]. Recently, simulations have been employed to discover promising monomer candidates for creating novel polyimides for capacitor applications [7, 23]. Here, DFT (density functional theory) calculations were used to simulate the dielectric properties of over 150.000 polymers and promising candidates were then selected for synthesis and experimental evaluation [23]. The experimental data correlated well with the properties predicted by the simulations, showing that this approach is a valid and fast method for finding new polymers for capacitor applications [7, 23].

Polyetherimide (PEI) exhibits quite promising properties. This polymer has a high dielectric constant, high temperature stability, is self healing and relatively cheap [3]. This makes PEI a promising candidate for future application as the

dielectric in polymer film capacitors. PEI is produced by several companies around the world under the brand name Ultem. It is widely applied, in food industry as well as in aerospace. Its fabrication and application is controlled by several norms [24–26]. Pfeiffenberger et al. found that PEI films could be used to manufacture capacitors with film thicknesses of 5 μm . The studied films show temperature stable BDS > 550 V/ μm (up to 150 °C) as well as stable permittivities (ca. 3.2) and dielectric losses (below 1.5 %) over frequency and temperature. Due to the thermal stability, capacitors with PEI films have been shown to be usable for mounting on PCBs (printed circuit boards) via solder reflow process [8]. Some efforts have been put into composite materials with PEI. Chen et al. suggested the addition of SiO₂ nanoparticles to improve the thermal, mechanical and dielectric properties of PEI [27]. It has been found that the maximum SiO₂ load, however, cannot exceed 2 vol%, without the polymer becoming brittle. Nevertheless, an improvement for the thermal and dielectric properties has been found for up to 10 vol% filler loading.

2.2 POLYMER BLENDS

Since tradeoffs need to be made with respect to the properties when using neat polymers for power capacitors, blending two or more polymers with different properties in the necessary ratios seems an obvious solution. Ferroelectric polymers based on poly(vinylidene fluoride) (PVDF) are of major interest, since they combine high permittivity with high energy densities, but their high losses [28, 29] are prohibitive for most power applications.

Aromatic polythiourea (ArPTU) is shown to possibly inhibit early polarization saturation in PVDF-crystals leading to higher breakdown strength while also increasing the permittivity and even lowering the losses [28]. PVDF can also be blended with PP in order to combine the high permittivity of PVDF with the good processability and low loss of PP, however since PVDF and PP are immiscible, a compatibilization agent like maleic anhydride grafted to PP may be used [30]. In other experiments, Polyamide 11 has been added to improve processability and dielectric properties of PVDF. Here, also a compatibilization agent (vinyl acetate-maleic anhydride) has been used to decrease losses and to increase permittivity [31]. Alternatively, low loss poly(ethylene-chlorotrifluoroethylene) (PECTFE) can be used to reduce the losses of PVDF. It has also been shown that by crosslinking the blends, high-field losses can be reduced even more due to lower interfacial polarization [32]. Blends of PVDF with HFP (hexafluoropropylene) and VDF-oligomers or copolymers with CTFE have been examined as well. Due to the increased breakdown strength higher energy densities of 15–27 J/cm³ were obtained [33, 34]. When adding TrFE (trifluoroethylene) and CFE (chlorofluoroethylene), the resulting terpolymer P(VDF-TrFE-CFE) shifts from ferroelectric to a ferroelectric relaxor behavior with very low remanent polarization which leads to large changes in electric displacement field (D) and therefore to a high energy density [29]. For ferroelectric relaxors, the main cause of dielectric

breakdown has been identified as an electromechanical breakdown mechanism consisting of Maxwell stress (compression due to Coulombic attraction of the electrodes) and electrostrictive stress due to conformational changes of the polymer chains [35].

One research group tested blending PP with polyaniline (PANI) but while an increase in permittivity was found with increasing filler content, also an increase of dielectric loss and a decrease of partial discharge (PD) resistance was found. Furthermore, dielectric breakdown strength tended to decrease for high filler concentrations [36, 37].

A different blending approach has also been proposed: combining a high breakdown strength material like polycarbonate with a material with a high dielectric constant like PVDF via microlayer coextrusion. This layered structure results in an increased dielectric breakdown field strength (BDS) caused by a barrier effect when compared to the neat polymers or blends thereof [38].

When looking at the different polymers considered for power capacitor applications, it becomes clear that there are many options to choose from. Some these polymers or blends might be better suited than others and they should therefore be more thoroughly investigated. It is the opinion of the authors that BOPP will – at least for some time – remain as the most used dielectric in power capacitors. This is mainly due to its low price but also due to the fact that factories and supply lines are already well established and the material is well understood. The main disadvantage of polymers like PVDF-CTFE is that halides are present. They may cause environmental danger during processing. This affects not only the price but may yield a future issue with respect to RoHS-conformity. PEI and PI are seen by the authors as good candidates for high-temperature power capacitor applications with high energy densities and low losses. These polymers should therefore be more closely studied. It is advisable to use simulations like Treich et al. [23] in order to find candidates with desirable properties in less time. One promising branch is thought to be the blending of polymers. However, the same statement as above has to be made about halogenated components. It probably would be advisable to investigate blends of temperature-resistant halogen-free polymers with PP and try to adapt the expertise for PP-film production to PP-blend processing.

3 NANOCOMPOSITES

Another approach in improving the dielectric properties of polymers is the incorporation of nanometer sized particles into the different polymers [39–42]. The electrical properties of composites of polymers and ceramic particles can usually be anticipated by mixing laws. This, however, only works well only for particles in the micrometer range or above, which have a low surface to volume ratio (specific surface). When particle sizes approach nanometer dimensions, effects of the surface of the particle and the interface/interphase with the surrounding polymer become dominant. Therefore, other models have to be employed. First, an overview of the

theoretical models for polymer nanocomposites (PNCs) will be given before discussing the experimental research on nanocomposites.

3.1 THEORIES ON NANOCOMPOSITES

A first theoretical approach explaining the behavior of nanoparticles in a solid dielectric was given by Lewis in 2004 [43]. He identified the interfacial volume as becoming the dominant feature when particle sizes drop below 200 nm. This is depicted in Figure 4. It is assumed that the particles are charged and that there are mobile ions present in the polymer matrix. Therefore, an electric double layer (Stern layer) is formed around the particles.

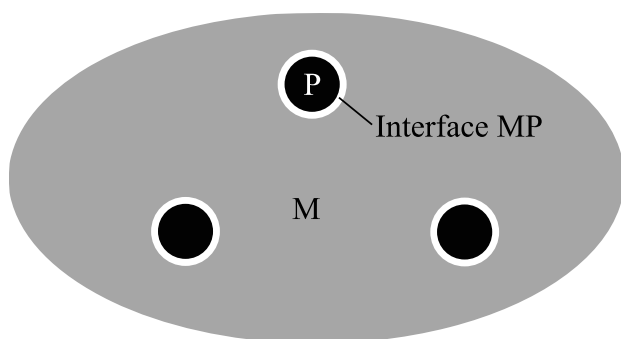
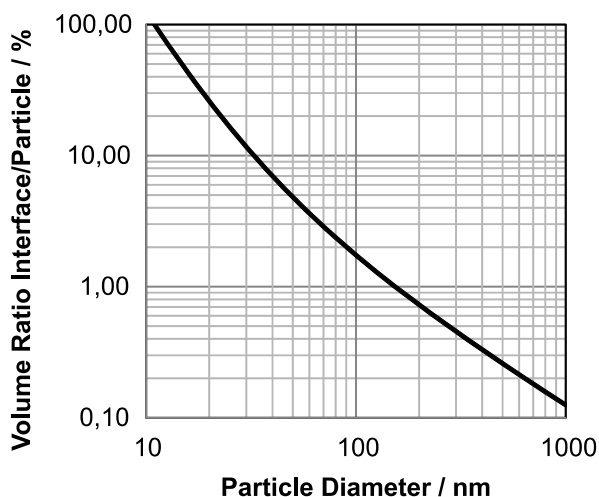


Figure 4. Percentage of the volume ratio of spherical nanoparticles P in a composite taken up by the interface MP as a function of the diameter d for a thickness of the interface of 20 nm (no agglomeration assumed); scheme according to [43].

When an electric field is applied, the nanoparticles behave like a large dipole as the charge carriers move along the interface due to their higher mobility compared to the host matrix. This induces polarization of the interface around the particles, which in turn leads to an increase in the effective permittivity of the compound exceeding the permittivity calculated with mixing rules. Losses, however, can also increase in this case because a diffusion cloud of charge carriers is formed around the nanoparticles, which oscillates out of phase with the applied field when the frequency is low. At high particle concentrations above the percolation

threshold, it is then possible for the double layers to overlap and form conducting channels in which charge carrier migration takes place [43]. This state is to be avoided when aiming for an application as insulation material.

Tanaka refined Lewis' theory by developing first a working hypothesis, the "multi-core model", to explain the behavior of polymer nanocomposites as dielectrics and electric insulators [44]. This model also identifies the interface between the polymer matrices and nano-fillers as the region responsible for the properties of nanocomposites. The multi-core model describes four different layers (see Figure 5). The first layer (about 1 nm in thickness) is a layer that is strongly bonded to the inorganic nanoparticle as well as to the organic polymer matrix. This layer can correspond with coupling agents like silanes. The second layer (several nanometers thick) describes an interfacial region where polymer chains are interacted either chemically or physically with the first layer and with the nanoparticle surface. The third layer (over 10 nm in thickness) is defined as a volume in which polymer chains are loosely coupled and interacted with the second layer. In this third region, the polymer matrix is altered with respect to chain conformation and regarding mobility as well as free volume and crystallinity. An electric double layer (a Gouy-Chapman diffuse layer) is superimposed on the three layers described above. This electric double layer is formed by the surface charge of the nanoparticles and a subsequent counter charge in the polymers that decays exponentially from the contact surface to the Debye shielding length (with a calculated thickness of about 30 nm) [44]. It is important to keep in mind that the thickness of the layers can vary for the different composites which influences the observed parameters [45]. The thickness of the bonded layer (first layer) has been found by others to be about 1 nm, too, e.g. [46, 47]. The thicknesses of the second and the third layer, respectively, can be inferred through application of Tanaka's model [45], however they cannot be precisely defined [48].

With the multi-core theory, experimental results, such as changes in permittivity, loss, low- and high field conduction, space charge mitigation, thermally stimulated current (TSC), dielectric breakdown strength, and partial discharge (PD) resistance can be explained [45, 49, 50].

Tanaka *et al* further suggest that nanoparticles interacting with charge carriers are not to be regarded as simple carrier traps but rather as quantum dots (QDs) with reduced or negative permittivity and Coulomb blockade effect. Since the charge carrier trap size is in the atomic range and since nanoparticles are substantially larger (in the nanometer range) and many properties of nanocomposites dielectrics can be explained, this concept seems to be valid. One particle might have several QDs of nanometer size on its surface (nanocrystals can be QDs) [51].

Another known deterioration mechanism is the formation of a so-called "electrical tree" before electric breakdown. This erosion mechanism is different from - but similar to - degradation through partial discharges. It describes the erosion of polymers in a network-like structure that visually resembles

the branches of a tree. Initial erosion of the polymer surface (“tree initiation”, or formation of a “tree bud”) may form branching channels (“tree growth”) into the bulk of the polymer. As it erodes, charring of the channel walls can occur, which causes these branches to exhibit increased conductivity that further promotes tree growth. Increases in treeing lifetime, i.e. resistance to tree growth, and PD resistance at low fields can be explained with the multi-core model as electrons interact with and are decelerated by electronic states (traps) in the third layer retarding the formation and length of tree buds [52, 53].

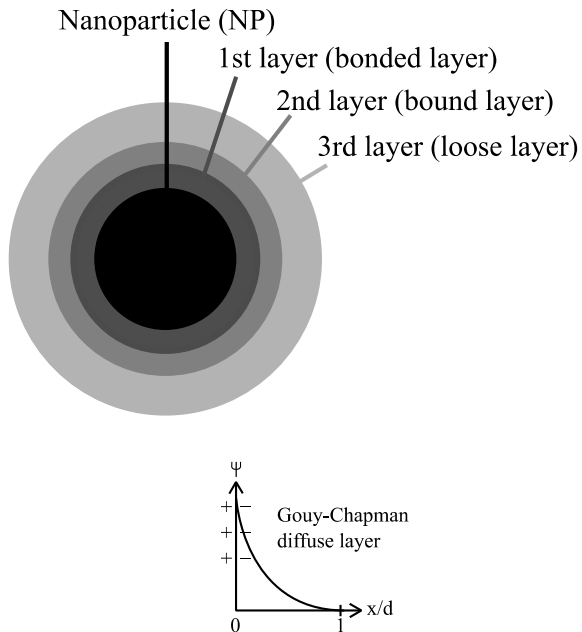


Figure 5. Different layers as described in Tanaka's multi-core model. Figure modified according to [44].

The assumption that the charge carrier density is different in each of the three layers described in the multi-core model has been confirmed by Liu et al., with the second layer having the highest trap density and lowest charge carrier mobility and the third layer having the highest charge carrier mobility. PI/Al₂O₃ nanocomposites were examined by the isothermal decay current (IDC) measurements and the small-angle x-ray scattering (SAXS) method [54]. The trap level distribution was evaluated using a modified isothermal discharge theory developed by Lei et al. [55]. SAXS was employed to find the electron density distribution in the interface, which is connected to the trap level and trap level density [54]. Smith et al. also confirmed that the interfacial region in nanocomposites is responsible for the change in electric properties and that these changes are mainly due to increased local conductivity and surface states of nanoparticles contributing to changes in mobility and charge carrier energy [56].

A potential barrier model has been proposed by Li. It shows similarities to the multi-core model. Here, however, an interaction zone is postulated as an independent region with a thickness of the transition region smaller than the free path of charge carriers. Low filler concentrations lead to carriers that

are restrained in the transition region, and as a result the dielectric strength increases. However, the permittivity decreases due to the increased free volume in the interaction zone and therefore dipoles are less mobile. When the filler concentration reaches the percolation threshold, conducting paths are formed due to overlapping interaction zones, increasing conductivity and reducing the dielectric breakdown strength [57].

Other developed models calculate the effective permittivity by approximating the composites as two-phase systems consisting of a complex particle (ellipsoidal nanoparticles with an interfacial shell) and the matrix. It has been found out that the permittivity of the composite increases when either the permittivity of the nanoparticles or the thickness of the interfacial shell increase or when the particles are more disc-shaped instead of ball-shaped [58].

Simulations have shown that “dangerous particle paths” leading to dielectric breakdown are statistically unlikely to form if particle or agglomerate sizes are kept below 1 μm and the filler volume fractions are kept at low values between 2 and 5 vol% when a typical capacitor film thickness of 10 μm is assumed [59]. This highlights the importance of good dispersion of nanoparticles in polymer matrices.

The incorporation of nanoparticles seems to be a proper way to improve the dielectric properties of polymers either by increasing the permittivity or the dielectric breakdown strength. In both cases the energy density of the dielectric material increases. In this review, Tanaka's multi-core model will be used as a basis for discussion, as it is one of the most widely accepted and used models concerning the electric properties of nanocomposites.

3.2 EXPERIMENTS ON NANOCOMPOSITES

Large varieties of particle systems as well as polymers have been used in studies to characterize the influence of nanometer-sized particles in polymer matrices. Since Polypropylene is the most widely used material for plastic film capacitors, it is also often used in studies on polymer nanocomposites (PNC) [60–62]. Polyethylene is also often used as a matrix for PNCs [11, 63, 64]. For its main application as cable insulation [65], the aim is to reduce the permittivity. This is contrary to the field of power capacitors, where the target is to increase the permittivity. One has, however, tried to influence dielectric loss and breakdown strength in the same manner as for capacitor applications [11, 63, 64]. Since from a chemical standpoint it is very similar to PP, experiments with PE-based nanocomposites should also be considered when investigating the advantages of utilizing nanoparticles for capacitor applications, despite PP is usually preferred due to higher operating temperatures at a competitive price. Due to the ease of preparation on a lab scale, epoxy is also often used as a model polymer to investigate the influence of nanoparticles on the dielectric properties of nanocomposites [66–68]. More recently, PVDF has also seen an increased interest for improvement with nanometer-sized fillers [69, 70]. Silica (SiO₂) is primarily used as a filler due to its inexpensiveness and since it is readily

available [60, 61, 71]. Barium Titanate (BaTiO_3) is also often used, especially for incorporation into PVDF due to its high permittivity [42, 70]. Other particle systems include Alumina (Al_2O_3) [72], Titania (TiO_2) [66–68] and Magnesia (MgO) [64]. Due to the high specific surface area of nanoparticles, low filler concentrations of below 10 wt% are used for most studies [39, 61, 66], whereas filler concentrations of up to 20 wt% [12] or even as high as 69 wt% [70] are investigated less often, but are also considered.

Since dielectric breakdown is a phenomenon that occurs on randomly distributed weak points of the dielectric material, Weibull statistical analysis may be employed to characterize this dielectric property. Usually a two-parameter cumulative distribution function is used (Equation (1)).

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

The variable x stands for the measured breakdown field. In equation (1), α denotes the scale parameter and β the shape parameter. 63.2 % of the breakdown population lies below α . β indicates the width of the distribution. The higher the β -value, the narrower is the distribution, i.e., the lower is the scattering. For high dielectric breakdown performance, high values for both α and β are necessary [73]. For practical capacitor design, however, high β -values are probably of greater relevance than high α -values, since breakdowns at low probability reduce the capacitor performance.

3.2.1 POLYPROPYLENE NANOCOMPOSITES

Dielectric Breakdown Field Strength:

Polypropylene-silica nanocomposites show increased dielectric breakdown strength at low filler contents, an effect which occurs more pronouncedly for dc loads rather than for ac loads (50 Hz and 60 Hz) [61, 71, 74]. As can be seen in Figure 6, an increase of 52 % in the α -value for dc fields and only 20 % for ac fields has been found by Takala et al. for BOPP filled with 5 wt% SiO_2 [74], while Bulinski et al. found a 12 % increase in ac breakdown field strength for 8 wt% SiO_2 in non-oriented PP films [71]. These differences, as well as the differences in the absolute values, might be related to a different sample preparation (biaxial orientation and no orientation, respectively) as well as to other measurement configurations (cylinder-plane and sphere-plane electrodes, respectively) as well as to different functionalization and possibly primary particle size. Other authors also found an increase in BDS for low concentrations of MgO [75], nanoclay [73], fluorohectorite [39], CaCO_3 [76] and Polyhedral Oligomeric Silsesquioxanes [77] in PP. Even if the increase in α is not as high, the β -values also increase with the filler content and the distributions of the BDS values become more narrow and less extreme low values occur [39, 61, 71, 73–77]. For the application as a dielectric for film capacitors, this in turn means that narrower safety margins could be defined and of the dielectric strength of the material could be better taken advantage. A critical filler size in the range of 100 nm has been proposed. Below that, the short-term BDS is not negatively affected by the nanoparticles [78].

With respect to the dc measurements of dielectric breakdown strength, it has been found that there is a dependence on the measurement area [79] as well as on the ramp rate [79, 80]. An increased measurement area leads to smaller α -values [79]. This may have been expected as randomly distributed weak points are more likely to have an effect, when greater areas are examined. BOPP films show higher dc-BDS with higher ramp rates. This ramp-rate dependency is even amplified for silica-filled BOPP. In this study, the α -values for breakdown were lower for filled BOPP – a phenomenon that is attributed to agglomerates [80]. Agglomerate effects might disguise the influence of space charge effects that can affect the breakdown behavior. Tanaka's multi-core theory postulates space charge mitigation by nanoparticles due to shallower energy levels of traps in the third layer [45]. From this, one can deduce that the ramp-rate-dependency should be less pronounced for nanofilled BOPP. Agglomerates affect, on the other hand, the breakdown behavior in complex ways [81]. Without TEM or SEM analysis for the used samples in [80], no clear conclusions as to the underlying mechanics of the observed ramp-rate-dependency can be made. It is notable that while for unfilled systems the shape parameter decreases with increasing ramp rate, for filled systems it first decreases but then increases again [80]. It was also found that the α -value for large area dc-tests decreases with the filler content but increases in case of ac-tests [82].

It has been proven that reprocessing of PP-nanocomposites and mixing with pristine composite can improve the dc-breakdown behavior, indicating recyclability of PP-nanocomposites without negative effects for capacitor applications [83]. A study on the ageing behavior confirms a similar behavior of nanocomposites to unfilled BOPP films with respect to the dielectric loss and to the large area dc-breakdown [84].

It should be pointed out that none of the studies mentioned above provided roughness measurements of the film surface, despite this has been proven to affect the dielectric breakdown of BOPP films [15] and to possibly distort the results.

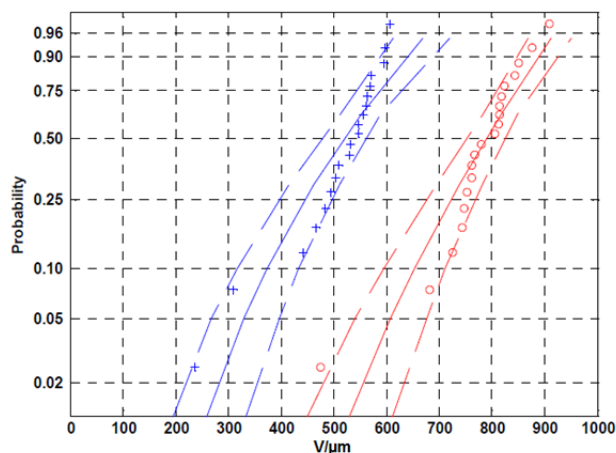


Figure 6. DC breakdown strength ($\text{V}/\mu\text{m}$) of PP reference (+) and PP + 5 wt% silica (o) presented in a Weibull probability plot. Both films were biaxially oriented. Reprint with permission of the authors from [74].

Permittivity and Dielectric Loss:

Real permittivity (ϵ_r') and loss tangent ($\tan\delta$) usually vary only moderately at low filler concentrations when compared to the base polymer. Takala and Ritamäki found that ϵ_r' increases and $\tan\delta$ remains at values of the unfilled polymer in PP with low filler content of surface modified silica [61, 74, 84, 85]. Since the first and the second layers of the multi-core model are considered to reduce the permittivity and the third layer is considered to increase it (as it contains dipoles and ionic carriers) [45], it is fair to state that in this case, the third layer is probably larger in volume than the first and second layers when considering the increase in permittivity. Since the increase is very slight and $\tan\delta$ seems to remain at values of the unfilled polymer, it is further concluded that the Maxwell-Wagner-Sillars (MWS)-polarization at the particle-matrix interface is not very pronounced. This argument is further strengthened by the fact that the permittivity difference between PP and silica is comparatively low and the good dispersion of the particles is due to hydrophobic surface groups. When non-surface modified silica is used, the dielectric losses tend to increase at low frequencies, probably due to water molecules at the interface [60]. When silicates or organoclays are added to PP, both permittivity and losses increase and relaxation peaks become evident in the loss tangent measurements that are attributed to MWS-polarization [86, 87]. Adding POSS can increase ϵ_r' and $\tan\delta$, depending on the used type [77].

DC-Conductivity:

It was found that if the nanoparticles have a high aspect ratio, the dc-conductivity of PP-nanocomposites may increase (i.e., the dc-resistivity may be negatively affected) due to overlapping diffuse double layers. However, looking at aged samples, the increase in dc-conductivity is less pronounced with increased filler contents [71].

Space Charge:

Space charge measurements are mostly conducted for PE-composites, but one work that investigated PP-composites found similar results, i.e., a reduction in bulk space charge [39]. The results for PE-nanocomposites are listed below and an explanation of the behavior shall be given.

Partial Discharge Resistance:

Partial discharge (PD) resistance shows a considerable increase – this means lower erosion speed – when polymers are filled with nanoparticles. This is not only true for filled PP systems but almost universally for most polymer nanocomposites [12, 48, 61, 66, 72, 73, 88–90]. It is thought to have several reasons that are met for most nanocomposites systems. Therefore, all systems will be addressed:

1. Nanoscale segmentation effect: finer segmentation results in stronger PD resistance (erosion tend to be slower for smaller nanoparticles)
2. Permittivity difference effect: electric field focuses on nanoparticles due to their higher permittivity when compared to the matrix

3. Coupling agent effect: tighter binding between matrix and nanoparticles results in improved PD resistance (first layer of the multi-core model has a major contribution)
4. Nanofiller pile-up effect: nanoparticles form a protective layer at the surface after the destruction of the polymer matrix due to PD erosion [66]

The last effect is shown schematically in Figure 7 and has been confirmed by optical microscope images [61] and by SEM and TEM analysis [89]. When partial discharge occurs, only the polymer is eroded. The inorganic particles then remain without polymer matrix, aggregate and “pile up”, forming sinter necks between each other due to a local increase in temperature during a PD event. With time, an insulating protective layer of inorganic particles is formed. It protects the underlying nanocomposites from further degradation through PD [89]. It has been found that the PD resistance can be increased up to 50 % for epoxy/silica and even doubled for PP/silica composites, as can be obtained Figure 8 [88]. Others found an increase in PD resistance for epoxy with increasing POSS-content due to a pile-up effect. A sevenfold increase was observed at very high filler loadings of 20 wt% [12]. This, however, comes at the price of decreasing BDS and increased dielectric losses due to the formation of crystalline regions and the resulting field distortion due to a permittivity mismatch, so again, the optimal filler content was found to be at a lower value of 2.5 wt% [12]. Nanofiller pile-up effect has also been proven in treeing experiments on epoxy/silica nanocomposites. There, it was found that the treeing growth is driven by partial discharges. Also higher filler content corresponded to increased PD resistance and in turn, slower tree propagation due to the formation of a protective oxide layer from the nanofiller in the tree channels was shown [91]. It was also put forth that the tree initiation rate decreases with the nanofiller content because of homogeneous charge formation around the needle-electrode tip which effectively increases the needle tip radius and thereby decreasing the effective electric field. This in turn decreases the number of discharge events [91].

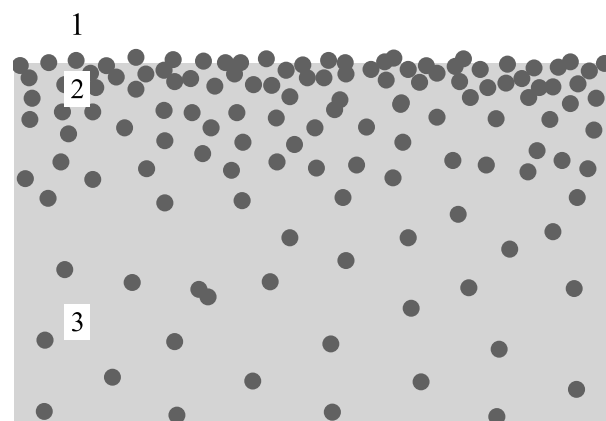


Figure 7. Nanofiller pile up effect - theoretical model with three different areas. 1: surrounding medium; 2: protective layer; 3: non-eroded, nano loaded polymer. Figure drawn according to the model in [89].

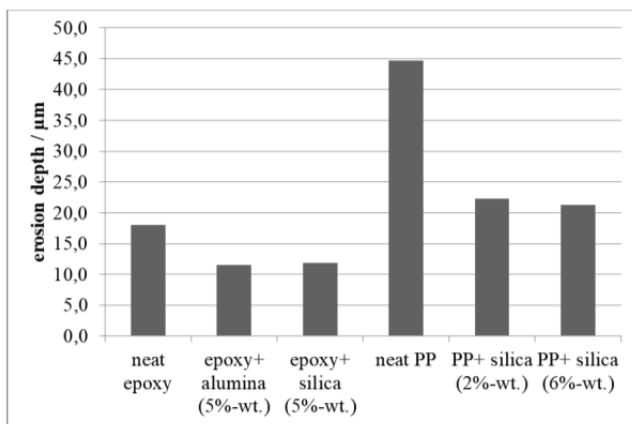


Figure 8. Erosion depth for polypropylene and epoxy nanocomposites at an aging time of 120 hours. Data collected from [88].

There are hints that the variation of the local field around particles affects the electric field in the composite and therefore influences the PD resistance (this addresses reason 2). At filler concentrations below the percolation threshold, the space charge does not accumulate as much as in higher filled systems above the percolation threshold (PP+6 wt% organosilicate in this study). Hence, the PD resistance first increases with the nanofiller content and then decreases above the percolation threshold [62]. A similar behavior has been found for LDPE+SiO₂ compounds [92].

Furthermore, the coupling effect has been confirmed with an 67 % increase of PD resistance for surface modified silica in comparison to non-modified silica in XLPE (cross-linked polyethylene) [48].

The segmentation effect has been proven by Tanaka et al. with epoxy nanocomposites [66, 72]. They also showed evidence for the permittivity difference effect by comparing the PD resistance of epoxy/silica and alumina nanocomposites with the more matched silica (lower permittivity) leading to higher PD resistance [72].

3.2.2 POLYETHYLENE NANOCOMPOSITES

Dielectric Breakdown Field Strength:

In few studies, the BDS decreases when nanofillers are added with surface modified silica fillers showing higher values than non-modified silica due to a better dispersion, e.g. [10]. Mostly however, it is found that both α - and β -values increase for filled PE and surface modified fillers perform superior compared to non-modified fillers [11, 48, 64, 65, 93, 94]. These improvements are attributed to the reduction of bulk charge accumulation as local conducting paths are formed by overlapping electric double layers around nanoparticles [11].

According to another interpretation, charge carrier scattering at the interfaces as well as the suppression of charge carrier acceleration due to the reduction of free volume may explain the increased BDS [64]. It has also been shown that nanocomposites are more susceptible to water uptake that decreases the dielectric strength. The degree of susceptibility is dependent on the functional groups grafted onto the

nanoparticles as well as on the conditioning of the samples [95].

Permittivity and Dielectric Loss:

Both, the permittivity and the loss tangent behave inconsistently for nano-filled XLPE in a study where samples were prepared in one location and were distributed for evaluation by different groups. Some labs found improved dielectric parameters, in other labs, more negative effects prevailed, but it is still unclear where these discrepancies come from [48]. Obviously, test conditions are very important for evaluating the dielectric behavior of insulating films.

Quasi-dc conduction (a sharp increase of the permittivity at low frequencies) has been observed for filled polyethylene at low frequencies due to charges migrating within the electric double layer around the particles inducing a polarization at the polar ends of particles, resulting in large dipoles with permittivities higher than those of the nanoparticles [11].

A study on water uptake of non-functionalized (hydrophilic) silica reported on two distinctive peaks in the loss spectra. The peak at lower frequencies was attributed to nanosilica/water/nanosilica interfaces within agglomerates, whereas the peak at higher frequencies was attributed to agglomerate/matrix interfaces [78].

DC Conductivity:

In contrast to Polypropylene, PE-composites show a decrease in dc-conductivity with increasing filler content. Surface modification amplifies this behavior [10, 48, 64]. When nanoparticles are added, trapping sites (quantum dots) are introduced in the polymers. They then reduce the mean free path of the charge carriers [64]. Nanoparticles are located near the surfaces of the polymers and can trap charge carriers that are injected from the electrodes. This yields in the formation of homocharges and inhibits further charge carrier injection. A lower charge carrier density in the sample bulk results and in turn a lower dc-conductivity follows [10, 51].

Space Charge:

It has been found that space charge injection as well as accumulation is strongly reduced for increased filler contents [10, 11, 48, 64, 93], with one exception where impurities of the filler were attributed to be the reason for a space charge increase [94]. It was also found that hetero charge is reduced and homo charge (space charge with the same polarity as the neighboring electrode) is injected when PE is filled with nanoparticles while only hetero charge (space charge with the opposite polarity to that of the neighboring electrode) is formed for the unfilled polymer [48]. The mitigation of space charge can be explained with the multi core model: nanoparticles introduce a shallow trap band that results in an increase in apparent carrier mobility. Whether the shallower energy level of these traps is due to an addition of new traps in the nanocomposites to or the replacement of the original traps present in pristine polymer through the new traps could yet not have been clearly worked out [45].

3.2.3 EPOXY NANOCOMPOSITES

Typically, epoxy nanocomposites are being characterized for electrical insulation applications but there is no intent on using them as dielectrics for capacitors, due to their mechanical properties and processability. Since epoxy nanocomposites can easily be prepared in laboratories, they are considered sometimes as model composites to evaluate the influence of nanofiller content and surface modification of the nanofillers. Therefore, they are reviewed here as well.

Dielectric Breakdown Field Strength:

Generally, the BDS increases for nanofilled (oxides and in one case functionalized Si-particles) epoxy with increasing filler content up to a certain filler concentration before decreasing again for higher filler content. It has also been found that surface modification positively affects the dielectric strength [12, 13, 96–98]. This behavior is attributed to the fact that nanofillers may act as additional cross-linking sites. This leads to a higher cross-linking density and therefore lowers the free volume. One may also consider the locally increased conductivity at the interfaces, which mitigates charge accumulation and in turn homogenizes the electric field [12]. The decrease of the α -value at higher filler concentrations is attributed to an increase in imperfections if the dispersion quality is low [97]. An increase in water uptake at the interface and the formation of imperfections at the interface [13] or the formation of crystalline zones (in the case of POSS) that result in a locally increased electric field and local charge accumulations at the interface [12] are also suggested to reduce the α -values. It was also found that bimodal surface functionalization of silica (i.e. two different molecules) can further increase (ac-)BDS when one species with long molecules increases dispersion and the other species with short molecules introduces electron trap sites [99].

In one study, however, no statistically significant increase could be found for epoxy/POSS-nanocomposites in ac breakdown strength. A possible increase in lightning impulse breakdown was hinted at, but could not be confirmed because of flash overs due to the measurement setting [100].

Permittivity and Dielectric Loss:

The permittivity and loss tangent increase with the addition of POSS-filler content due to the higher ϵ_r' of the filler and due to increased localized charge movement and MWS-polarization especially at low frequencies and high filler contents [12, 45, 90]. It can be concluded that good dispersion is achieved if no additional relaxation peaks are found in the dielectric loss spectra [12]. At low filler concentrations, ϵ_r' usually decreases due to the restriction of polymer chain movement in the first and second layer of the multi-core model [45, 90, 98].

3.2.4 PVDF NANOCOMPOSITES

Poly(vinylidene fluoride), PVDF, which is a ferroelectric polymer, and its ferroelectric copolymers like poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) usually filled with high-permittivity nanoparticles like BaTiO₃ are often

investigated aiming to find composites with a very high energy density [40, 101].

Dielectric Breakdown Field Strength:

The dielectric breakdown field strength for PVDF-based composites first increases when nanofillers are added, for instance in the form of spherical particles or nanowires with a high aspect ratio. Above a certain filler content BDS, however, decreases [40, 42, 102, 103]. Again, this is attributed to the mitigation of bulk charge and the suppression of interfacial polarization at low filler concentrations and to the introduction of imperfections like voids at high filler loadings [40, 102].

Permittivity and Dielectric Loss:

ϵ_r' usually increases greatly if nanofillers are added, while $\tan(\delta)$ either remains independent or increases only slightly [40, 42, 42, 101, 103–105]. The permittivity is mainly considered as an effect of the formation of the ferroelectric β -phase and of the high permittivity of the filler [40], while the good performance with respect to losses can be explained by the suppression of space charges. In addition, interfacial sites may trap charge carriers [101].

Hydroxylated and carboxylated graphene was dispersed in PVDF as well. Significant higher values for the permittivity were found, whereas the losses remained low. So-called “micro-capacitors” were assumed to form with the result of a higher overall permittivity, i.e., nanosheets with –OH-groups prevent agglomeration and small spaces between single sheets that are oppositely charged form. They form the “micro-capacitors”, if the low percolation threshold of 0.2 wt% has been reached [106].

A significant increase in permittivity in conjunction with relatively minor decreases in BDS lead to a significant increase in energy storage density of up to 21 J/cm³. Such high values were only found for very high filler loadings (50 vol%) of BaTiO₃ particles with paraffin shells. These compounds however show high residual polarization, which leads to elevated losses during the discharging of a capacitor film. This results in very low discharged energy density and low efficiency ($\eta = J_{re} / (J_{re} + J_{loss})$ where J_{re} is the recoverable energy density and J_{loss} is the energy loss [107]) of the capacitor film of only 10 % [70]. A comparable energy density of 20.5 J/cm³ with a significantly higher energy efficiency of 60 % was found for a tri-layered structure with PVDF/boron nitride nanosheets as outer layers and PVDF/barium strontium titanate nanowires as central layer [103].

3.2.5 OTHER NANOCOMPOSITES

In a study where polystyrol (PS) was directly grafted onto BaTiO₃-nanoparticles to form core-shell particles, it was found that dielectric losses remain at low values while the permittivity significantly increases. Also, no relaxation peaks were found due to the absence of interfacial polarization [108]. When poly(methyl methacrylate) (PMMA) is directly grafted onto BaTiO₃ particles, the permittivity also increases while losses remain low. Additionally, BDS increased slightly

when compared to pure PMMA. Altogether, a higher energy density was achieved [14].

In a similar study, silica particles with polymer grafted to the surface (assembled to form a composite with homogenous interparticle distance) were compared to classically blended PS-PMMA/SiO₂ composites. Here, the permittivity increased also and losses remained low for the assembled nanoparticle-composites, while losses increased significantly for traditionally blended composites. This results in a higher energy density and in an improved efficiency for the assembled nanoparticle-composites compared to the classically blended composites due to superior dispersion of nanoparticles [109].

The effect of high-temperature dielectrics where thermally crosslinked divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) was formed with boron nitride nanosheets (BNNS) being present, was investigated as well. It was shown that such a c-BCB/BNNS composite was superior to other high-temperature polymers like PEI, PV, PEEK or Kapton with regard to energy density and charge-discharge efficiency due to a reduction of high field leakage current at elevated temperatures [41].

In another study, multi-walled carbon nanotubes (MWCNTs) coated with polypyrrole were used as nanofillers for polystyrene in order to increase the energy density. It was found that the organic coating was very effective for ensuring a good dispersion of the MWCNTs in the matrix as well as for preventing percolation at low filler concentrations. The latter would lead to low BDS and high losses. Filler contents of 0.1 %-wt. up to 10 %-wt. with pure PS samples as reference were investigated. It was found that the permittivity increased up to 44 with increasing filler content while losses remained at acceptable levels (< 0.07). However, it was also found out that the BDS decreased with increasing filler content so that the highest energy density of 4.95 J/cm³ was found at 8 %-wt. MWCNT-content [110].

4 SUMMARY

Table 2 overviews the change in the dielectric properties for the most commonly investigated polymer matrices, under the precondition that only small amounts of nanofillers are added. The arrows indicate strong increase (upwards arrow), medium increase (northeast arrow), no change (horizontal arrow) or medium decrease (southeast downwards arrow) of the respective property. Question marks indicate that the influence of nanoparticles is highly inconsistent.

Table 2. Influence of low nanofiller content on the dielectric parameters of polymer matrices.

	PP	PE	Epoxy	PVDF
BDS	↑	↑	↑	↗
ϵ_r'	↗	?	↘	↑
$\tan(\delta)$	→	?	→	↗

As a condensed conclusion, one may summarize that low contents of nanofillers generally increase the BDS, if the filler is well dispersed and if no percolation of the layers around particles with increased conductivity occurs to form conducting paths through overlapping layers between neighboring particles. Dielectric losses may increase when adding nanofillers or remain at levels very close to the base polymer, but a significant decrease can be ruled out. The influence of nanofillers on the permittivity depends on the specific combination of materials at hand and has a complex dependency with the surface functionalization of the nanofiller as well as the permittivities of the materials and the filler concentration.

5 FUTURE

Many improvements of polymer dielectrics have been achieved over the last years by incorporating nanometer-scaled fillers into polymer matrices. However, there are still many open questions before these materials can be employed for large-scale production for power capacitors in converter stations or in offshore wind farms. Especially, the economic aspect of scaling-up the production to industrial volumes is to be carefully considered, as some of the nanofillers can be very expensive (e.g. BaTiO₃), whereas others may be rather inexpensive (e.g. SiO₂). This should be kept in mind when conducting research on composites targeting to an industrial application. Considering the fact that flexible films of several μm thickness have to be used for capacitors, it becomes clear that epoxy-based systems are not well suited due to their rigidity and owing to the fact that they cannot be melt-processed like thermoplastics. Epoxy-based systems, however, can and will still be used as model systems to study nanoparticle-matrix-interaction on a laboratory scale since samples can be easily prepared.

As mentioned above PVDF-based systems are disadvantageous due to their relatively high price as well as RoHS-conformity issues may remain in the future. This should always be kept in mind, but it is possible that these systems become competitive if major advantages over state-of-the-art BOPP films can be made. Today, BOPP-based nanocomposites show the most promising results for improvements of dielectrics for capacitor applications. This is because both the matrix material and the manufacturing processes are understood and commonly available. The incorporation of nanofillers on an industrial scale would require only few adaptations of the already existing manufacturing processes. Improved BDS would decrease film thicknesses and therefore yield smaller capacitors with the same applied voltages. Reduced size with the same power, however, will influence the thermal management in the capacitor, which has to be evaluated with life-sized demonstrator capacitors. If thermal management proves to be difficult, improvement of thermal conductivity of the composites should be investigated.

One topic that should also further investigated is, the influence of nanoparticles on polymer matrices that has not

been fully theoretically understood. More effort should be spent on understanding interfacial effects and the behavior of nanocomposites on a microscopic level.

So far, in most studies that are dealing with dielectric breakdown phenomena, the surface roughness of films has not been taken into account. One can easily imagine that a high surface roughness can decrease the breakdown field strength, as the thickness at certain spots of the film can decrease significantly. This may lead to a lower breakdown voltage (and the thickness is overestimated at this spot, which leads to a lower calculated field). Therefore, in order to achieve comparable results, roughness of samples should be recorded when characterizing the BDS. If the roughness of filled and unfilled systems is vastly different, the observed responses are a combination of material properties and measurement equipment and do not reflect pure material properties.

In addition, round robin tests of new nanofiller materials are recommended.

ACKNOWLEDGMENT

The authors would like to thank the German Federal Ministry for Economic Affairs and Energy for funding this work under grant number 03ET7559B.

REFERENCES

- [1] T. R. Jow et al., "Pulsed power capacitor development and outlook," *IEEE Pulsed Power Conf. (PPC)*, 2015, pp. 1–7.
- [2] M. Rabuffi and G. Picci, "Status quo and future prospects for metallized polypropylene energy storage capacitors," *IEEE Trans. Plasma Sci.*, vol. 30, no. 5, pp. 1939–1942, 2002.
- [3] D. Tan, L. Zhang, Q. Chen, and P. Irwin, "High-Temperature Capacitor Polymer Films," *Journal of Elec Materi*, vol. 43, no. 12, pp. 4569–4575, 2014.
- [4] EPCOS AG, A TDK Group Company, Product Catalogue 2017.
- [5] T. Tanaka and T. Imai, "Advances in nanodielectric materials over the past 50 years," *IEEE Electr. Insul. Mag.*, vol. 29, no. 1, pp. 10–23, 2013.
- [6] X. Peng et al., "Development of high dielectric polyimides containing bipyridine units for polymer film capacitor," *Reactive and Functional Polymers*, vol. 106, pp. 93–98, 2016.
- [7] R. Ma et al., "Rationally designed polyimides for high-energy density capacitor applications," (eng), *ACS applied materials & interfaces*, vol. 6, no. 13, pp. 10445–10451, 2014.
- [8] N. Pfeifferberger et al., "High temperature dielectric polyetherimide film development," *IEEE Trans. Dielect. Electr. Insul.*, vol. 25, no. 1, pp. 120–126, 2018.
- [9] J. Ho and T. R. Jow, "Effect of crystallinity and morphology on dielectric properties of PEEK at elevated temperature," *IEEE Int' Conf. on Solid Dielectr. (ICSD)*, 2013, pp. 385–388.
- [10] S. Ju, M. Chen, H. Zhang, and Z. Zhang, "Dielectric properties of nanosilica/low-density polyethylene composites: The surface chemistry of nanoparticles and deep traps induced by nanoparticles," *Express Polym. Lett.*, vol. 8, no. 9, pp. 682–691, 2014.
- [11] M. Roy et al., "Polymer nanocomposite dielectrics - the role of the interface," *IEEE Trans. Dielect. Electr. Insul.*, vol. 12, no. 4, pp. 629–643, 2005.
- [12] T. Heid, M. Frechette, and E. David, "Enhanced electrical and thermal performances of nanostructured epoxy/POSS composites," *IEEE Trans. Dielect. Electr. Insul.*, vol. 23, no. 3, pp. 1732–1742, 2016.
- [13] R. Kochetov et al., "The effect of nanosilica on the DC breakdown strength of epoxy based nanocomposites," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2014 pp. 715–718.
- [14] S. A. Paniagua et al., "Surface-initiated polymerization from barium titanate nanoparticles for hybrid dielectric capacitors," (eng), *ACS applied materials & interfaces*, vol. 6, no. 5, pp. 3477–3482, 2014.
- [15] I. Rytöluoto, A. Gitsas, S. Pasanen, and K. Lahti, "Effect of film structure and morphology on the dielectric breakdown characteristics of cast and biaxially oriented polypropylene films," *European Polymer J.*, vol. 95, pp. 606–624, 2017.
- [16] S. Laihonen, U. Gafvert, T. Schutte, and U. Gedde, "DC breakdown strength of polypropylene films: Area dependence and statistical behavior," *IEEE Trans. Dielect. Electr. Insul.*, vol. 14, no. 2, pp. 275–286, 2007.
- [17] K. M. Slenes, P. Winsor, T. Scholz, and M. Hudis, "Pulse power capability of high energy density capacitors based on a new dielectric material," *IEEE Trans. Magn.*, vol. 37, no. 1, pp. 324–327, 2001.
- [18] N. Zhang, J. Ho, J. Runt, and S. Zhang, "Light weight high temperature polymer film capacitors with dielectric loss lower than polypropylene," *J Mater Sci: Mater Electron*, vol. 26, no. 12, pp. 9396–9401, 2015.
- [19] Z.-H. Dai et al., "Increased dielectric permittivity of poly(vinylidene fluoride-co-chlorotrifluoroethylene) nanocomposites by coating BaTiO₃ with functional groups owning high bond dipole moment," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 529, pp. 560–570, 2017.
- [20] M. Zaccaria, C. Gualandi, D. Fabiani, M. L. Focarete, and F. Croce, "Effect of Oxide Nanoparticles on Thermal and Mechanical Properties of Electrospun Separators for Lithium-Ion Batteries," *J. Nanomaterials*, vol. 2012, pp. 1–8, 2012.
- [21] L. Zheng et al., "Preparation of PVDF-CTFE hydrophobic membranes for MD application: Effect of LiCl-based mixed additives," *J. Membrane Science*, vol. 506, pp. 71–85, 2016.
- [22] R. K. Goyal, K. A. Rokade, and A. S. Kapadia, "Study on novel high performance polymer nanocomposites for electronics packaging paper," *Int. Conf. Nanoscience, Engineering and Technology (ICONSET)*, 2011, pp. 376–380.
- [23] G. M. Treich et al., "A rational co-design approach to the creation of new dielectric polymers with high energy density," *IEEE Trans. Dielect. Electr. Insul.*, vol. 24, no. 2, pp. 732–743, 2017.
- [24] Aerospace; polyetherimide (PEI) semi-finished products and moulded parts; technical specification, 65498, 1991.
- [25] Classification System and Basis for Specification for Polyetherimide (PEI) Materials, 2016.
- [26] Specification for Extruded and Compression-Molded Shapes Made from Polyetherimide (PEI), 2012.
- [27] B.-K. Chen, C.-T. Su, M.-C. Tseng, and S.-Y. Tsay, "Preparation of Polyetherimide Nanocomposites with Improved Thermal, Mechanical and Dielectric Properties," *Polym. Bull.*, vol. 57, no. 5, pp. 671–681, 2006.
- [28] W. Li, L. Jiang, X. Zhang, Y. Shen, and C. W. Nan, "High-energy-density dielectric films based on polyvinylidene fluoride and aromatic polythiourea for capacitors," *J. Mater. Chem. A*, vol. 2, no. 38, pp. 15803–15807, 2014.
- [29] B. Chu et al., "A dielectric polymer with high electric energy density and fast discharge speed," (eng), *Science (New York, N.Y.)*, vol. 313, no. 5785, pp. 334–336, 2006.
- [30] Z.-M. Dang, W.-T. Yan, and H.-P. Xu, "Novel high-dielectric-permittivity poly(vinylidene fluoride)/polypropylene blend composites: The influence of the poly(vinylidene fluoride) concentration and compatibilizer," *J. Appl. Polym. Sci.*, vol. 105, no. 6, pp. 3649–3655, 2007.
- [31] D. Kuang, R. Li, and J. Pei, "Polyamide 11/Poly(vinylidene fluoride)/Vinyl Acetate-Maleic Anhydride Copolymer as Novel Blends Flexible Materials for Capacitors," *Polymers*, vol. 6, no. 8, pp. 2146–2156, 2014.
- [32] S. Wu, M. Lin, S. G. Lu, L. Zhu, and Q. M. Zhang, "Polar-fluoropolymer blends with tailored nanostructures for high energy density low loss capacitor applications," *Appl. Phys. Lett.*, vol. 99, no. 13, p. 132901, 2011.
- [33] K. Yao et al., "Nonlinear dielectric thin films for high-power electric storage with energy density comparable with electrochemical supercapacitors," *IEEE Trans. Ultrasonics, Ferroelectrics, and Frequency Control*, vol. 58, no. 9, pp. 1968–1974, 2011.
- [34] X. Zhou, B. Chu, B. Neese, M. Lin, and Q. Zhang, "Electrical Energy Density and Discharge Characteristics of a Poly(vinylidene fluoride-chlorotrifluoroethylene) Copolymer," *IEEE Trans. Dielect. Electr. Insul.*, vol. 14, no. 5, pp. 1133–1138, 2007.
- [35] J. Claude, Y. Lu, K. Li, and Q. Wang, "Electrical Storage in Poly(vinylidene fluoride) based Ferroelectric Polymers: Correlating Polymer Structure to Electrical Breakdown Strength," *Chem. Mater.*, vol. 20, no. 6, pp. 2078–2080, 2008.

- [36] K. Kannus, P. Harju, K. Lahti, J. Pelto, and M. Pajanen, "Electrical properties of polypropylene and polyaniline compounds," *IEEE Int. Conf. Solid Dielectrics (ICSD)*, 2004, pp. 67–70.
- [37] M. Takala, T. Sallinen, Nevalainen, J. Pelto, and K. Kannus, "Surface Degradation of Nanostructured Polypropylene Compounds Caused by Partial Discharges," *IEEE Int. Symp. Electr. Insul. (ISEI)*, 2008, pp. 205–209.
- [38] M. Mackey et al., "Enhanced breakdown strength of multilayered films fabricated by forced assembly microlayer coextrusion," *J. Phys. D: Appl. Phys.*, vol. 42, no. 17, p. 175304, 2009.
- [39] G. C. Montanari et al., "Modification of electrical properties and performance of EVA and PP insulation through nanostructure by organophilic silicates," *IEEE Trans. Dielect. Electr. Insul.*, vol. 11, no. 5, pp. 754–762, 2004.
- [40] Y. Hou, Y. Deng, Y. Wang, and H. Gao, "Uniform distribution of low content BaTiO₃ nanoparticles in poly(vinylidene fluoride) nanocomposite: Toward high dielectric breakdown strength and energy storage density," *RSC Adv*, vol. 5, no. 88, pp. 72090–72098, 2015.
- [41] Q. Li et al., "Flexible high-temperature dielectric materials from polymer nanocomposites," (eng), *Nature*, vol. 523, no. 7562, pp. 576–579, 2015.
- [42] G. Wang, X. Huang, and P. Jiang, "Tailoring Dielectric Properties and Energy Density of Ferroelectric Polymer Nanocomposites by High-k Nanowires," (eng), *ACS applied materials & interfaces*, vol. 7, no. 32, pp. 18017–18027, 2015.
- [43] T. J. Lewis, "Interfaces are the dominant feature of dielectrics at the nanometric level," *IEEE Trans. Dielect. Electr. Insul.*, vol. 11, no. 5, pp. 739–753, 2004.
- [44] T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, "Proposal of a multi-core model for polymer nanocomposite dielectrics," *IEEE Trans. Dielect. Electr. Insul.*, vol. 12, no. 4, pp. 669–681, 2005.
- [45] T. Tanaka, "Dielectric nanocomposites with insulating properties," *IEEE Trans. Dielect. Electr. Insul.*, vol. 12, no. 5, pp. 914–928, 2005.
- [46] N. Fuse, M. Kozako, T. Tanaka, S. Murase, and Y. Ohki, "Possible mechanism of superior partial-discharge resistance of polyamide nanocomposites," *IEEE 17th Annu. Meeting Lasers and Electro-Optics Society (LEOS)*, 2004, pp. 322–325.
- [47] J. K. Nelson, J. C. Fothergill, L. A. Dissado, and W. Peasgood, "Towards an understanding of nanometric dielectrics," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2002, pp. 295–298.
- [48] T. Tanaka et al., "Dielectric properties of XLPE/SiO₂ nanocomposites based on CIGRE WG D1.24 cooperative test results," *IEEE Trans. Dielect. Electr. Insul.*, vol. 18, no. 5, pp. 1482–1517, 2011.
- [49] T. Tanaka, "Promising Characteristics of Nanocomposite Dielectrics," *IEEE 8th Int. Conf. Properties Appl. Dielectr. Mat. (ICPAM)*, 2006, pp. 12–22.
- [50] T. Tanaka, "Interpretation of Several Key Phenomena Peculiar to Nano Dielectrics in terms of a Multi-core Model," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2006, pp. 298–301.
- [51] T. Tanaka, "A novel concept for electronic transport in nanoscale spaces formed by islandic multi-cored nanoparticles," *IEEE Int. Conf. Dielectr. (ICD)*, 2016, pp. 23–26.
- [52] T. Tanaka, "Buds for treeing in epoxy nanocomposites and their possible interaction with nano fillers," *IEEE 10th Int. Conf. Solid Dielectrics (ICSDS)*, 2010, pp. 1–4.
- [53] T. Tanaka, "Similarity between treeing lifetime and PD resistance in aging mechanisms for epoxy nanocomposites," *IEEE Int. Conf. Prop. Appl. Dielectr. Mat. (ICPADM)*, 2009, pp. 741–744.
- [54] Y.-Y. Liu et al., "Research of Trap and Electron Density Distributions in the Interface of Polyimide/Al₂O₃ Nanocomposite Films Based on IDC and SAXS," *Chinese Phys. Lett.*, vol. 34, no. 4, p. 48201, 2017.
- [55] Q. Lei, F. Tian, C. Yang, L. He, and Y. Wang, "Modified isothermal discharge current theory and its application in the determination of trap level distribution in polyimide films," *J. Electrostatics*, vol. 68, no. 3, pp. 243–248, 2010.
- [56] R. Smith, C. Liang, M. Landry, J. Nelson, and L. Schadler, "The mechanisms leading to the useful electrical properties of polymer nanodielectrics," *IEEE Trans. Dielect. Electr. Insul.*, vol. 15, no. 1, pp. 187–196, 2008.
- [57] S. Li, G. Yin, S. Bai, and J. Li, "A new potential barrier model in epoxy resin nanodielectrics," *IEEE Trans. Dielect. Electr. Insul.*, vol. 18, no. 5, pp. 1535–1543, 2011.
- [58] Q. Xue, "Effective dielectric constant of composite with interfacial shells," *Physica B: Condensed Matter*, vol. 344, no. 1–4, pp. 129–132, 2004.
- [59] A. an Ling and S. A. Boggs, "What is "Nano" in the Context of a Filled Dielectric?" *IEEE Int. Symp. Electr. Insul. (ISEI)*, 2006, pp. 273–276.
- [60] H. Couderc, M. Frechette, and E. David, "Fabrication and dielectric properties of polypropylene / silica nano-composites," *IEEE Electr. Insul. Conf. (EIC)*, 2015, pp. 329–332.
- [61] M. Takala et al., "Dielectric properties and partial discharge endurance of polypropylene-silica nanocomposite," *IEEE Trans. Dielect. Electr. Insul.*, vol. 17, no. 4, pp. 1259–1267, 2010.
- [62] P. Basappa et al., "An investigation into the effect of varying the main field and local field on the PD characteristics of nanofilled polypropylene films," *IEEE Electr. Insul. Conf. (EIC)*, 2015, pp. 247–250.
- [63] F. Ciuprina, I. Plesa, P. V. Notingher, T. Tudorache, and D. Panaitescu, "Dielectric Properties of Nanodielectrics with Inorganic Fillers," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2008, pp. 682–685.
- [64] J. Yang et al., "Effects of Interfacial Charge on the DC Dielectric Properties of Nanocomposites," *J. Nanomaterials*, vol. 2016, no. 5, pp. 1–11, 2016.
- [65] A. T. Mohamed, "Experimental enhancement for dielectric strength of polyethylene insulation materials using cost-fewer nanoparticles," *Int. J. Electr. Power Energy Sys.*, vol. 64, pp. 469–475, 2015.
- [66] T. Tanaka and T. Iizuka, "Generic PD resistance characteristics of polymer nanocomposites," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2010, pp. 1–4.
- [67] J. K. Nelson, Y. Hu, and J. Thiticharoengpong, "Electrical properties of TiO₂/sub 2/ nanocomposites," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2003, pp. 719–722.
- [68] J. K. Nelson and J. C. Fothergill, "Internal charge behaviour of nanocomposites," *Nanotechnology*, vol. 15, no. 5, pp. 586–595, 2004.
- [69] Y. Thakur, M. H. Lean, and Q. M. Zhang, "Reducing conduction losses in high energy density polymer using nanocomposites," *Appl. Phys. Lett.*, vol. 110, no. 12, p. 122905, 2017.
- [70] D. Zhang et al., "High energy density in P(VDF-HFP) nanocomposite with paraffin engineered BaTiO₃ nanoparticles," *Sensors and Actuators A: Phys.*, vol. 260, pp. 228–235, 2017.
- [71] A. Bulinski, S. S. Bamji, M. Abou-Dakka, and Y. Chen, "Dielectric properties of polypropylene loaded with synthetic organoclay," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2009, pp. 666–671.
- [72] T. Tanaka et al., "Dielectric properties and PD resistance of epoxy/fumed and precipitated silica and alumina nanocomposites," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2012, pp. 279–282.
- [73] A. B. Poda, R. Dhara, M. A. Rab, and P. Basappa, "Evaluation of aging in nanofilled polypropylene by surface discharges," *IEEE Trans. Dielect. Electr. Insul.*, vol. 23, no. 1, pp. 275–287, 2016.
- [74] M. Takala et al., "Dielectric Properties of Polypropylene-Silica Nanocomposites," *Nordic Insul. Symp. (NORD)*, 2009, pp. 31–35.
- [75] W. Cao, Z. Li, G. Sheng, and X. Jiang, "Insulating property of polypropylene nanocomposites filled with nano-MgO of different concentration," *IEEE Trans. Dielect. Electr. Insul.*, vol. 24, no. 3, pp. 1430–1437, 2017.
- [76] M. Takala, S. Kortet, P. Salovaara, M. Karttunen, and K. Kannus, "AC Breakdown Strength of Polypropylene-Calcium Carbonate Compounds," *Nordic Insul. Symp. (NORD)*, 2007, pp. 123–126, 2007.
- [77] M. Takala et al., "Dielectric properties of nanostructured polypropylene-polyhedral oligomeric silsesquioxane compounds," *IEEE Trans. Dielect. Electr. Insul.*, vol. 15, no. 1, pp. 40–51, 2008.
- [78] H. Couderc, E. David, and M. Frechette, "Study of Water Diffusion in PE-SiO₂ Nanocomposites by Dielectric Spectroscopy," *Trans. Electr. Electron. Mat.*, vol. 15, no. 6, pp. 291–296, 2014.
- [79] I. Rytoluoto et al., "Large-area dielectric breakdown performance of polymer films – Part II: Interdependence of filler content, processing and breakdown performance in polypropylene-silica nanocomposites," *IEEE Trans. Dielect. Electr. Insul.*, vol. 22, no. 4, pp. 2196–2206, 2015.
- [80] I. Rytoluoto, M. Ritamaki, K. Lahti, and M. Karttunen, "DC ramp rate effect on the breakdown response of SiO₂-BOPP nanocomposites," *IEEE 11th Int. Conf. Prop. Appl. Dielectr. Mat. (ICPADM)*, 2015, pp. 496–499.
- [81] T. Krentz et al., "Morphologically dependent alternating-current and direct-current breakdown strength in silica-polypropylene nanocomposites," *J. Appl. Polym. Sci.*, vol. 134, no. 1, p. 812, 2017.
- [82] M. Ritamaki, I. Rytoluoto, M. Niittymäki, K. Lahti, and M. Karttunen, "Differences in AC and DC large-area breakdown behavior of polymer thin films," *IEEE Int. Conf. Dielectr. (ICD)*, 2016, pp. 1011–1014.

- [83] I. Rytoluoto, M. Ritamaki, K. Lahti, S. Pasanen, and J. Pelto, "Dielectric breakdown properties of mechanically recycled SiO₂-BOPP nanocomposites," *IEEE Int. Conf. Dielectr. (ICD)*, 2016, pp. 288–292.
- [84] M. Ritamaki et al., "Large-area approach to evaluate DC electro-thermal ageing behavior of BOPP thin films for capacitor insulation systems," *IEEE Trans. Dielect. Electr. Insul.*, vol. 24, no. 2, pp. 826–836, 2017.
- [85] M. Takala et al., "Effect of low amount of nanosilica on dielectric properties of polypropylene," *IEEE 10th Int. Conf. Solid. Dielectr. (ICSD)*, 2010, pp. 1–5.
- [86] M. Ambid et al., "Effect of filler concentration on dielectric behaviour and on charge trapping in PP/clay nanocomposites," *17th Annu. Meeting IEEE Lasers and Electro-Optics Society (LEOS)*, 2004, pp. 389–392.
- [87] E. Izci and N. Bowler, "Dielectric properties of isotactic polypropylene and montmorillonite nanocomposites," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2010, pp. 1–4.
- [88] T. Iizuka and T. Tanaka, "Comparison of partial discharge resistance of several nanocomposites," *Elect. Eng. Jpn.*, vol. 182, no. 1, pp. 1–9, 2013.
- [89] C. Meichsner et al., "Formation of a protective layer during IEC(b) test of epoxy resin loaded with silica nanoparticles," *IEEE Trans. Dielect. Electr. Insul.*, vol. 19, no. 3, pp. 786–792, 2012.
- [90] A. Krivda et al., "Characterization of epoxy microcomposite and nanocomposite materials for power engineering applications," *IEEE Electr. Insul. Mag.*, vol. 28, no. 2, pp. 38–51, 2012.
- [91] W. Yang, X. Yang, M. Xu, P. Luo, and X. Cao, "The effect of nano SiO₂ additive on electrical tree characteristics in epoxy resin," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2013, pp. 683–686.
- [92] Aulia, Z. Abdul-Malek, Y. Z. Arief, M. A.M. Piah, and M. Jaafar, "Partial Discharge Characteristic of Low Density Polyethylene and Silica Nanocomposite," *AMM*, vol. 554, pp. 133–136, 2014.
- [93] M. Roy, J. K. Nelson, L. S. Schadler, C. Zou, and J. C. Fothergill, "The influence of physical and chemical linkage on the properties of nanocomposites," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2005, pp. 183–186.
- [94] F. Guastavino et al., "Electrical characterization of polymer-layered silicate nanocomposite," in *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2005, pp. 175–178.
- [95] I. L. Hosier, M. Praeger, A. F. Holt, A. S. Vaughan, and S. G. Swingler, "On the effect of functionalizer chain length and water content in polyethylene/silica nanocomposites: Part I — Dielectric properties and breakdown strength," *IEEE Trans. Dielect. Electr. Insul.*, vol. 24, no. 3, pp. 1698–1707, 2017.
- [96] W. Sun, H. Wu, X. Tan, M. R. Kessler, and N. Bowler, "Silanized-silicon/epoxy nanocomposites for structural capacitors with enhanced electrical energy storage capability," *Composites Science and Technology*, vol. 121, pp. 34–40, 2015.
- [97] M. Gao, P. Zhang, F. Wang, L. Li, and Z. Li, "The relationship between dielectric properties and nanoparticle dispersion of nano-SILICA/Epoxy composites," *Annu. Rep. Conf. Electr. Insul. Dielectr. Phenom. (CEIDP)*, 2013, pp. 234–237.
- [98] H. Li et al., "Effects of silane coupling agents on the electrical properties of silica/epoxy nanocomposites," *IEEE Int. Conf. Dielectr. (ICD)*, 2016, pp. 1036–1039.
- [99] S. Virtanen et al., "Dielectric breakdown strength of epoxy bimodal-polymer-brush-grafted core functionalized silica nanocomposites," *IEEE Trans. Dielect. Electr. Insul.*, vol. 21, no. 2, pp. 563–570, 2014.
- [100] M. Takala et al., "Thermal, mechanical and dielectric properties of nanostructured epoxy-polyhedral oligomeric silsesquioxane composites," *IEEE Trans. Dielect. Electr. Insul.*, vol. 15, no. 5, pp. 1224–1235, 2008.
- [101] J. Li, J. Claude, L. E. Norena-Franco, S. I. Seok, and Q. Wang, "Electrical Energy Storage in Ferroelectric Polymer Nanocomposites Containing Surface-Functionalized BaTiO₃ Nanoparticles," *Chem. Mater.*, vol. 20, no. 20, pp. 6304–6306, 2008.
- [102] X. Zhang et al., "Ultrahigh energy density of polymer nanocomposites containing BaTiO₃@TiO₂ nanofibers by atomic-scale interface engineering," (eng), *Advanced materials (Deerfield Beach, Fla.)*, vol. 27, no. 5, pp. 819–824, 2015.
- [103] F. Liu et al., "High-Energy-Density Dielectric Polymer Nanocomposites with Trilayered Architecture," *Adv. Funct. Mater.*, vol. 27, no. 20, p. 1606292, 2017.
- [104] C. Behera, R. N. P. Choudhary, and P. R. Das, "Development of multiferroic polymer nanocomposite from PVDF and (Bi_{0.5}Ba_{0.25}Sr_{0.25})(Fe_{0.5}Ti_{0.5})O₃," *J Mater Sci: Mater Electron*, vol. 28, no. 3, pp. 2586–2597, 2017.
- [105] Y. Feng et al., "Enhanced dielectric properties of PVDF-HFP/BaTiO₃ - nanowire composites induced by interfacial polarization and wire-shape," *J. Mater. Chem. C*, vol. 3, no. 6, pp. 1250–1260, 2015.
- [106] C. Yang, S.-J. Hao, S.-L. Dai, and X.-Y. Zhang, "Nanocomposites of poly(vinylidene fluoride) - Controllable hydroxylated/carboxylated graphene with enhanced dielectric performance for large energy density capacitor," *Carbon*, vol. 117, pp. 301–312, 2017.
- [107] X. Hao, J. Zhai, and X. Yao, "Improved Energy Storage Performance and Fatigue Endurance of Sr-Doped PbZrO₃ Antiferroelectric Thin Films," *J. American Ceramic Society*, vol. 92, no. 5, pp. 1133–1135, 2009.
- [108] K. Yang et al., "Core-shell structured polystyrene/BaTiO₃ hybrid nanodielectrics prepared by in situ RAFT polymerization: A route to high dielectric constant and low loss materials with weak frequency dependence," (eng), *Macromolecular rapid communications*, vol. 33, no. 22, pp. 1921–1926, 2012.
- [109] C. A. Grabowski et al., "Performance of dielectric nanocomposites: Matrix-free, hairy nanoparticle assemblies and amorphous polymer-nanoparticle blends," (eng), *ACS applied materials & interfaces*, vol. 6, no. 23, pp. 21500–21509, 2014.
- [110] C. Yang, Y. Lin, and C. W. Nan, "Modified carbon nanotube composites with high dielectric constant, low dielectric loss and large energy density," *Carbon*, vol. 47, no. 4, pp. 1096–1101, 2009.

Maximilian Streibl was born in Bayreuth, Germany in 1991. He received Diploma degree from the University of Bayreuth, Germany, in 2016. He then joined Siemens AG, Munich, Germany and is pursuing his doctoral degree while working in the research group Functional Materials and Materials Processing. His research interests include nanodielectrics, materials for power storage and impedance spectroscopy.

Roman Karmazin was born in Brno, Czech Republic and received his doctoral degree on macromolecular chemistry from Technical University of Brno, Czech republic. He joined Siemens AG, Munich, Germany in 2006 and currently works there as an engineer in the research group Functional Materials and Materials Processing. His research interests include functional materials, especially ceramics and ceramics composite materials, as well as electronic devices. He is an author and coauthor of number of publications on field of functional ceramic materials and their applications.

Ralf Moos was born in Karlsruhe, Germany, in 1963. He received the Diploma degree in Electrical Engineering from the University of Karlsruhe, Germany, in 1989 and the doctoral degree from the same university with a thesis on the influence of donor dopants in strontium titanate on the electrical properties and defect chemical modelling in 1994. From 1995–2001 he was with Daimler AG, in Stuttgart and Friedrichshafen, Germany and was responsible for gas sensing. In July 2001, he was appointed head of the Department of Functional Materials at the University of Bayreuth. Key aspects of the research work at the Department of Functional Materials are mainly inorganic functional materials and polymer-oxide composites and devices and systems that are made thereof. With respect to materials, perovskites, porous framework materials (e.g., zeolites), and ion conductors are in the focus. Application fields encompass chemical sensors, catalysts, and materials for energy conversion. Special attention is given to film and layer technologies. As it is typical for an engineering research department, industrial applicability of the applied techniques and methods is of special importance.