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Citation: Fréchette, M. F., Vijh, A., Utracki, L., Trudeau, M. L., Sami, A., Laurent, C., Morshuis, P., Andritsch, T., Kochetov, R., Vaughan, A., et al (2010). Nanodielectrics: A panacea for solving all electrical insulation problems? In: 2010 10th IEEE International Conference on Solid Dielectrics (ICSD). (pp. 1-29). IEEE. ISBN 978-1-4244-7945-0 doi: 10.1109/ICSD.2010.5568067

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Nanodielectrics

A Universal Panacea for Solving All Electrical Insulation Problems ?

*by an international collective of scientists**

Prologue

At times new paradigms are observed to emerge. One example of this concerns the introduction of the concept of “Nanodielectrics” in 2001. It is often demeaned that with new concepts must come new ways of thinking, opened-minded consideration and unbounded exploration. In this spirit, an activity of high-creative intensity was organized at Hydro-Québec’s research institute (IREQ) on October 31st, 2008. A very diversified crowd of international scientists gathered at IREQ to exchange and reflect on the topic. An opportunity to be seized to break the established precincts and, to question and imagine the potentialities.

Provocative at times, the comments and views were only meant to elicit the progress of our thinking. The present paper does not summarize the proceedings of the event that came to be known as the “Brainstorm at the institute”. This paper offers a broad and diverse view of the topic, with many remaining questions of importance and feeded by recent progress and further reflection. Although long, the paper gives a vivid picture of the situation allowing criticism and stressing the many unanswered questions. Multidisciplinary zest is obvious.

Most of the participants joined in this new adventure. The list of authors is given at the end with an indication of their respective contribution. In view of the great number of authors, no effort was undertaken to reconcile the styles. The end product is a result of a participatory effort, and every bit does not need to be guaranteed and accepted by all.

The paper benefited particularly from the contributions of some scientists stranger to the usual field, namely A. Vijh, L. Utracki and H. Alamdari. AshokVijh joined us with his background in electrochemistry and has enlightened us with analogies of other fields concepts and applications (Chapter II). Leszek Utracki, a polymer scientist of many talents, has taught us by linking the polymeric context of nanocomposites to the dielectric properties. He has produced Chapter III. This would have been a logical determining cobblestone just after the introduction of the concept in 2001. This somewhat warranted a welcomed longer contribution. Finally, Houshang Alamdari is back in the mist of academic research. He was associated with the nanodielectrics from the beginning. For this paper, he introduced a non-electrotechnical application based on a nanodielectric material (Chapter VIII, section B).

*Michel F. Fréchette, Varennes, March 2010
IREQ - 40 ans de savoir et d’énergie*

*Nanodielectrics; polymer nanocomposites; electrical insulation;
solid dielectrics*

I. NANODIELECTRICS

When the nanodielectric concept was introduced [1] in 2001, it stemmed from a reaction to the great stir surrounding the nanostructuration of crystalline materials. What was in it for the insulation arena? Was there an equation of the sort “Nanotechnology + Dielectrics” equals something like a nanomaterial with affected dielectric properties?

Already, towards the end of the 90s, we had identified the aerogel and variants as 3-dimensional nanodielectrics. Also, some works pointed at nanoceramics exhibiting peculiar behaviours. Despite the fact that upon sintering, nanometric-size grains grow in dimensions, particular effects if not benefits from initial mixtures into ceramics of nanocomponents and additives had emerged. The major step taken in 2001 was proposing special dielectricity for polymer nanocomposites. A dielectric behaviour shaped, dictated or affected from a nanoscale manipulation. An account of the development of the concept was published last year [2]. In the emergence of the concept, the seminal work by John Lewis was recognized. Dielectricity at the nanoscale is thought to play a major role in determining the macroscopic upscale of the phenomena.

Although so far a major research effort has taken shape on nanodielectrics, it was dominated by the influence of polymer nanocomposites. In this framework, interfaces (as well explained by Lewis [3]) are dominant. However, the concept of nanodielectric [4] is more general than this. Eventually, when the degree of self-assembly will be mastered, insulating solids of revolution including polymers shall be constructed in which interfaces as well as building blocks will interplay.

A nanodielectric is by definition “a multi-component dielectric possessing nanostructures, the presence of which lead to changes in one of several of its dielectric properties”. The novelty is still in its infancy. Potentiality has been blurred for instances by the quality control of the polymer nanocomposites and/or the effects of sintering involving nanoceramics. But the future is ahead. Despite the difficulties, partial nanostructuration of polymer nanocomposites were found to improve partial-discharge resistance, to suppress space charge formation and affect charge relaxation, and to prolong the treeing lifetime [5, 6]. Many times, it remains a mystery how to change many properties at the same time. Especially considering that for an electrotechnical application, the material must satisfy a matrix of properties. Many of these properties are not dielectric.

Apart from opening the possibility to tailor dielectric properties and improve performance in some instances, some outstanding and novel behaviour were already observed. Giant permittivity [7] falls into this category. Although still under

scrutiny, there is evidence for an electrical microstructure consisting of semiconducting grains and insulating grain boundaries. It would seem that the low-achieved degree of self-assembly [8] for now precludes the observation of more novelties. In this direction, progress in the design and use of dendrimers [9] and, for instance, new techniques of sintering at low temperature (see for instance in [10]) will be instrumental in the near future.

For the next steps of development, force is to mention that nanofillers exhibiting extraordinary properties will draw some more attention. It is one of the approaches in order to provoke real emergence of novelty and/or marked deviations from extrapolated property improvement. To mention a few, carbon nanotubes [11] with or without encapsulation, silica flakes or graphene planes [12], insulating nanotubes like Boron Nitride [13] fall into this category. It is an area of research that shows promises.

The future lies ahead. The wealth of information on so many aspects presented in the following sections points indeed at the existence of a future for the field involving the nanostructuring of dielectrics.

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II. SOME PHYSICO-CHEMICAL CONSIDERATIONS ON NANOMATERIALS INCLUDING NANODIELECTRICS

Nanotechnology is the new growing frontier involving most areas of science and engineering. Almost every country has some sort of national nanotechnology initiative.

Nanotechnology is the research and development at the atomic, molecular or macromolecular levels in the sub-100 nm range (~ 0,1 - 100 nm) to create structures, devices and systems that have novel functional properties. Other definitions of nanotechnology have also been proposed but they all focus more or less on the 0,1 - 100 nm range with some variations which are not central to the present discussion.

Nanomaterials are thus defined as the substances and constituents, invariably solids, which are used to make the devices and structures in the 0,1-100 nm range. Such nanomaterials possessing interesting and useful dielectric properties are called nanodielectrics, which are the focus of the present review. These are invariably solid materials and are usually used as composites in which a small quantity of nanoparticles of one material (e.g. an oxide) is embedded within the main body of another dielectric material, e.g. a polymer.

A. Basic Physicochemical Nature of a Nanomaterial and its Consequences

A nanomaterial is dominated by the presence of grain boundaries over grains, i.e. over fifty percent of the solid is constituted by line defects (i.e. grain boundaries) and these interphasial regions (between the grains) are constituted by atoms having bonding (lower coordination number) that leads to high surface energy, high reactivity, low stability (e.g. tendency to sinter under high-field or temperature conditions), easy precipitation of impurities, strong chemisorption, and higher ionic conduction, etc. than the grains.

Importantly, novel functional properties arise in such materials owing to their nanosize; such properties usually have their origins in quantum mechanical effects which exhibit themselves at such levels of miniaturization. Thus "nano" does not just denote "miniaturization" – such miniaturization must lead to novel functions and properties. For example, when a nanomaterial particle approaches lower size limit of around 40 Å, quantum mechanical effects dominate creating totally new material properties, e.g. Pt particles of that size exhibit a pseudo band-gap and thus reduced electron density and catalytic properties. Gold particles of that size, on the other hand, show higher catalytic activities for reasons not altogether clear at the present time, although it may have to do with the spd hybridization under quantized conditions. In semiconductor quantum dots and quantum wells, the quantum confinement of electrons and holes arises at the nano-level which gives rise to novel device properties.

In "chips", when integrated circuits are printed with the distances between components and connections approaching 1-3 nm (10 to 30 Å), there is a "cross-talk", a sort of quantum interference. This represents the ultimate limit on miniaturization in circuit printing on chips. There are many more examples, e.g. Josephson junctions in which "nano" thickness of the oxide layers are involved through which the tunnelling cur-

rents pass; this, of course, is a quantum effect. A more spectacular example which is extremely speculative, is the basis of consciousness: how a piece of meat (i.e. brain) thinks? At the microtubules level in the neurons and other brain tissues, there are quantum transfer events at the nano and sub-nano scales, e.g. work of Roger Penrose [1] at Oxford University and Stuart Hameroff [2] at the University of Arizona (Tucson) and that of Litt [3].

B. Nanomaterials as Nanodielectrics: Problems and Promise

The reactive grain boundaries that dominate a nanomaterial including a nanodielectric would be expected to lead to pronounced heterogeneity of the material with the following consequences (as dielectric materials): i) high frequency dispersion; ii) high leakage currents; iii) high dielectric loss; iv) accelerated « ageing », i.e. deterioration of dielectric properties with time owing to temperature, field or current induced sintering; v) tendency to adsorb impurities and their precipitation at the reactive sites.

On the other hand, high reactivity of these materials would herald their use in: sensors; catalysts (gas phase reactions); electrocatalysts as in fuel cells, batteries, photoelectrochemical cells, super capacitors; pollution control devices, etc.

However, their use as dielectric materials as such would be limited because of expected high leakage currents and dielectric losses.

Notwithstanding these limitations, a great deal of work is being carried out in formulating composite insulating materials of commercial interest in which particles of nanodielectrics are embedded within a commonly used dielectric material such as polyethylene. For example, the group of L.S. Schadler at RPI in the USA has found that such a procedure yields insulating materials having improved breakdown strength, both at room temperature and at elevated temperatures. Other workers have also made similar observations [4,5]. What is the origin of this improved breakdown strength?

To understand the conceptual foundations of such an improvement, it is important to observe first that the percentage of embedded nanoparticles must be quite low (<1%). This is because of the low nanoparticle percolation threshold [4], particularly for the commonly-used particles. If the nanoparticle content increases beyond the percolation threshold, the nanoparticle tends to lose its beneficial effects. This arises because the nanoparticles act as a sort of hindrance to the propagation of electron avalanches found during dielectric breakdown, below the percolation threshold limit; this hindrance tends to be short-circuited above the threshold limit.

That the nanoparticles behave as barriers for electron propagation can be looked at from different conceptual angles as follows:

1) Nanoparticles because of their extended surface area change the very nature of the polymer, alter the depth and density of trap sites in the language of solid state physics, thus reducing charge carrier mobility and energy.

2) The structure between the polymer and the nanoparticle is the key to the trapping mechanism; this is where the charge

layer (the “double layer” – see below) develops and nanoparticles present an elongated scattering path to the charge carriers.

3) Since the area of interfaces between the nanoparticles and the polymer is very large, the whole polymer matrix may be essentially treated as the interfacial region. The outcome is a set of strengthened nanometric double layer interfaces [5]. These are electrochemical interfaces within which the highest fields can be sustained [5].

Finally, the most fundamental issue is that nanoparticles embedded (distributed) in a dielectric matrix create an enormous number of nanoscopic electrochemical interfaces and the interphasic regions thus created determine most, if not all, the features of nanodielectrics. The most notable feature thus developed is the enhancement of dielectric strength (or breakdown voltage in engineering jargon). However, one would also expect other concomitant effects such as higher dielectric losses, leakage currents, ageing effects associated with “electrolytic” migration of charged particles and other effects from a system in which heterogeneity has been deliberately introduced and electrochemical double layers have been purposefully developed.

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III. DIELECTRIC PROPERTIES OF POLYMERIC NANOCOMPOSITES

This section describes the components of polymeric nanocomposites (PNC), how these are prepared and what elements of their structure impact on dielectric properties. There are three principal PNC ingredients: polymeric matrix, nanoparticles and intermediary components, labelled as intercalants, surfactants, compatibilizers, etc.

A. PNC Components

1) Polymeric matrix.

From the growing concern for the environment comes a need for polymer recycling, what leads to a progressive replacement of thermosets by thermoplastics. This tendency first affected the classical composites (e.g., epoxy/glass fiber), then polymer blends and now the PNC [1, 2]. Accordingly, this text will emphasize the PNCs based on thermoplastics, especially on polyolefins (PO) such as the commodity polyethylenes (PE) and isotactic polypropylene (PP). These polymers are semi-crystalline with relatively low melting point and may be processed at temperatures, $T \leq 250^\circ\text{C}$. PO's are inexpensive, but degradable by physical (UV irradiation), chemical (oxidation) and mechanical (chain scission) means.

2) Nanoparticles.

In the IUPAC nomenclature, the nano-sized particles must have at least one dimension in the nano-meter range ≤ 2 nm. The nanoparticles may be one-, two-, or three-dimensional, but the industrial interest focuses on one-dimensional thin plates with much larger lateral dimensions [3]. These are mainly clays with platelets 0.7 – 2.5 nm thick [4]. Recently, layered double hydroxides (LDH) have been introduced [5].

The most frequently used are natural phyllosilicate clays. These are made of one octahedral layer (Oc) sandwiched between two tetrahedral (Tc) ones, *e.g.*, montmorillonite (MMT), hectorite (HT), or saponite (ST). Neither the chemical composition nor the crystalline structure of clay is constant. Contaminating atoms enter into the layers modifying clay properties. For example, in MMT substitution of Al^{+3} in Oc by Mg^{+2} introduces 0.25 to 1.2 negative charges per unit cell (the cation exchange capacity, CEC ≈ 0.5 to 2 meq/g) and a commensurate number of exchangeable cations, which are essential for the clay ability to fully disperse (exfoliate). If Al^{+3} are replaced by Fe^{+3} there is no change of electron balance, but the clay color changes what in turn results in brownish PNC.

In addition to natural clays, a variety of synthetic and semi-synthetic clays have been used. The prime advantage of these materials is control of purity and stability of their chemical composition. They also can be in situ intercalated, avoiding a cumbersome step. The PNC containing synthetic clay are white and can be dyed to any color and its intensity [4].

Little is known about the size, shape of individual clay platelet, their distribution, variability of chemical composition and impurities. Next, a short summary of results obtained by the VAMAS TWA-33 summarizes the present knowledge.

a) Shape, size and size distribution of clay platelets.

The three orthogonal dimensions of clay platelet are thickness ($t \approx 1$ nm), length (L) = the longest platelet dimension and perpendicular to it width (W). For the tested clays the ratio: $L/W \approx 1.5 \pm 0.2$, thus one may discuss only L . In natural clays L follows the Gaussian distribution with mean value ≈ 290 nm. For synthetic and semi-synthetic clays this dimension is significantly larger, *viz.* 1200 and 870 nm, respectively [6].

b) Chemical composition of clays.

The chemical composition of clay particles was measured using the energy-dispersive X-ray spectroscopy (SEM-EDS). Because clay may have locally-diverse composition, it is important that the measurements are repeated at least 30 times per specimens. The statistical error of the chemical composition in natural and synthetic clay was found to range from 10 to 5% of the mean value [7].

c) Impurities.

Natural clays are contaminated by organic (humic) substances, non-expandable clays (*e.g.*, amorphous clay, vermiculite, kaolin) and diverse particulate minerals [1]. For the use in PNC they are laboriously purified in about 300 steps. However, according to the pertinent patent, the resulting sodium clay still contains up to 5 wt% of impurities (amorphous silicates, stacks of welded platelets and the residual solid particles

with diameter > 300 nm) [1, 8]. The commercial, purified clay has 7 wt% of organics, hygroscopic and bound water, carbonic acid, etc.

Two clays have been analyzed for impurities; the natural sodium-MMT (Cloisite[®]-Na, or C-Na for short) and semi-synthetic fluoromica (Somasif ME100). In C-Na 13 mineral contaminants were found: Vermiculite, Quartz, Cristobalite, Rutile, Albite, Microcline, Aragonite, Vaterite, Dolomite, Gypsum, Anhydrite, Alunite, Sylvite. Production of ME100 starts with natural talc and sodium fluoro silicates. In the semi-synthetic fluoromica small quantities of Vermiculite and Gypsum were found, probably brought in with talc [9].

3) Intercalants and Compatibilizers [1].

After purification the clay sodium salt is highly hydrophilic and as such it may be exfoliated in water, forming thermodynamically miscible PNC with such water-soluble polymers, as polyethylene oxide, polyvinyl alcohol or polyvinyl pyridine; unsuitable for dielectric applications. As already mentioned, the preferred polymers for such use are hydrophobic PO's, PE or PP, which are thermodynamically immiscible with clay. The problem may be resolved by converting sodium clays into hydrophobic organoclays by reacting it with suitable intercalant. When this modification is insufficient for miscibility, the system may be compatibilized.

Most commercial intercalants are ammonium salts, $R_iN^+Cl^-$ where R_i are organic groups, some of which should be miscible with the polymer. For PNC with PO-type matrix, the clay may be intercalated with *di*-methyl *di*-hydrogenated tallow ammonium chloride (2M2HT) such as Cloisite[®] 20A (C20A). The tallow radicals (from beef fat) are long paraffinic and olefinic chains. After hydrogenation, the saturated chains ($\sim 65\%$ C_{18} , $\sim 30\%$ C_{16} and $\sim 5\%$ C_{14}) are expected to be miscible with low molecular weight PO.

In addition to making the clay hydrophobic, intercalation also expands the interlayer spacing (from about 1.2 up to *ca.* 3 nm) facilitating inter-diffusion of macromolecular chains, which results in enhanced platelets dispersion. For maximization of the interlayer spacing, one may use stoichiometric quantity of intercalant having large R_i groups. However, since these may block access to polymer molecules, the prefer strategy is the use of excess of intercalant. This strategy also has negative aspects as it increases PNC degradability and conductivity, decreasing modulus.

Since the PNC ingredients are polydispersed, the polymer-organoclay interactions are influenced by many factors. Only using molecular simulation one may determine the effects of a single factor. Thus, simulation indicates that the ionic charges are not located in specific points of clay platelet surface, but rather they are delocalized, smeared over large areas. Consequently, the intercalant is also spread on the surface at thickness dependent on its quality and quantity [10].

Incorporation of organoclay into polymer matrix results in good dispersion only in systems with strong polymer/clay interactions, such as those observed for polyamides (Nylons). However, for PNC based on PO, usually compatibilization is required. This has been accomplished by incorporation of a compatibilizer, prepared by functionalisation of the same type

of PO as that forming the matrix. Molecular simulation shows that efficiency of the process depends on the concentration, molecular weight and compatibilizer type [11, 12].

B. Preparation of PNC Samples for Dielectric Measurements

1) Compounding.

The clay-containing PNC have been prepared by the following methods (in chronological order):

- Reactive (*in situ* polymerization by polymer manufacturers)
- Solution (dispersing the organoclay in a polymer solution)
- Melt compounding (by compounders and part-makers).

Melt compounding is the preferred method that was used for the preparation of PNC samples for dielectric tests.

The three PNC ingredients are listed in Table I. PP has been used frequently in power capacitors, cable insulation, and in layer and phase separators for rotating electrical equipment and in transformers [13]. Polybond 3150 (PP-MA), was the compatibilizer. The organoclay C-20A is Wyoming MMT intercalated with 2M2HT.

The master batch (MB) method of compounding has been selected [14]. Accordingly, PP with 20 wt% PP-MA compatibilizer was dry-blended with Ciba antioxidant, Irganox B-225. The composition was fed from the main hopper to a co-rotating twin-screw extruder (TSE) while 10 wt% of organoclay was supplied from a side feeder. The materials were compounded under blanket of dry N₂ at $T = 200^{\circ}\text{C}$, screw speed $N = 200$ rpm and throughput $Q = 5\text{kg/h}$. The MB was palletized for the use in the subsequent dilution step, which reduced the organoclay concentration to 0, 1, 2 and 4 wt%. The weight ratio of the compatibilizer-to-organoclay content was kept constant at 2:1.

2) Formation.

The PNC samples for dielectric test need to have uniform thickness of $135 \pm 5 \mu\text{m}$ and smooth surface. The following two-step forming method was selected. First, diluted PNC compositions were extruded at $T = 180 - 230^{\circ}\text{C}$ into blown films. Next, these were flattened in a 3-rolls calender at 115°C .

Table I. PNC ingredients

Component	Trade name	M _w (kg/mol)	Density (g/mL)	T _m (°C)	Supplier
PP	ProFax HL-451H (PP)	250	0.902	~161	Basell Polyolefins
Maleated-PP	Polybond 3150 (0.5% MAH)	330	0.91	~164	Chemtura Corp.
Organoclay	Cloisite® 20A, C-20	---	---	---	Southern Clay Products

3) Clay dispersion.

Three methods were used for assessing the degree of clay dispersion in the PNC films: the X-ray diffraction method (XRD), the Field Emission Gun Scanning Electron Microscopy (FEGSEM) and the transmission electron microscope (TEM). XRD measures d_{001} – the interlayer spacing in regularly spaced clay stacks. However, it does not “see” the individual clay platelets or those in twisted or deformed stacks. For this reason the additional electron micrographs of different magnification are essential.

For PNC with isotactic PP as the matrix, the interlayer spacings is small, $d_{001} = 3.00 - 3.72$ nm, decreasing with concentration. The micrographs show that most clay is in short stacks of intercalated platelets, thus the desired random dispersion of exfoliated platelets was not achieved. However, it is noteworthy that PP is highly crystalline polymer in which the clay platelets are concentrated in the non-crystalline regions, where high concentration decreases the interlayer spacing. It was shown that the interlayer spacing linearly decreases with increasing organoclay content ($C15$) and crystallinity, (X), both in wt%, viz.:

$$d_{001} \text{ (nm)} = 10.5 - 0.392 C15 - 0.111 X \quad (1)$$

Accordingly, the interlayer spacing in amorphous PP extrapolated to infinite dilution should be fully exfoliated [15].

C. Example of the PNC Dielectric Properties

Various electric and dielectric test methods have been used in the preliminary studies of the clay effects in the PP-based PNC conducted within the VAMAS TWA-33 research program. These included space charge distribution measurements using the Pulsed Electro-Acoustic (PEA) method, the short-term electrical aging effects on breakdown strength (E_{BD}) by applying a ramp AC or DC voltage of 400-500 V/s to the specimen placed in silicon oil, DC polarizability and conductivity measurements at -10 kV/mm for detecting the charging and discharging currents, dielectric loss at power frequency using several types of ultra precision capacitive bridges for wide frequency (0.01 mHz – 20kHz), electroluminescence emission (EL), partial discharge resistance measurements, electrical erosion tests, etc. [16-22].

1) Space charge vs. clay content and aging time.

The total quantity of charge as function of aging time, $t_a = 0 - 500$ hrs is displayed in Figure 1.

In the case of neat PP, the homocharge injected from both electrodes accumulated in the central area, increasing with aging. In the case of PNC with 2 or 6 wt% organoclay, the heterocharges formed in the vicinity of both electrodes, initially increasing with aging time and then stabilizing.

For neat PP the undesirable space charge increases with time for at least 500 hrs. Incorporation of 2 wt% organoclay dramatically changed this behaviour – only during the first 24 hrs aging the charge increased and then it became constant, at the level significantly lower than that of neat PP. In PNC with 6 wt% organoclay initially the space charge was about 60% smaller than that in neat PP and 50% smaller than in PNC with

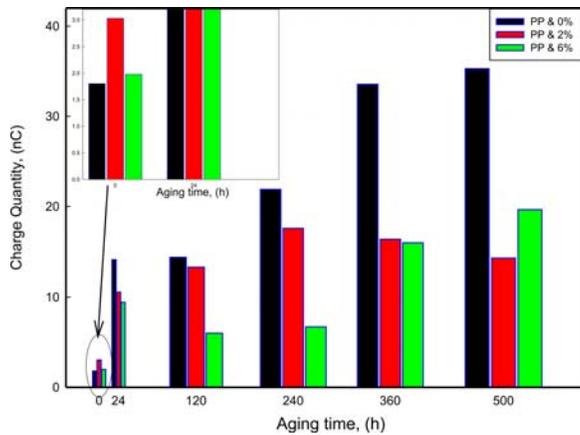


Figure 1. Charge vs. aging time for PNC containing 0, 2 and 6 wt% organoclay [17, 20].

2 wt% organoclay. However, after aging for 360 hrs its value became similar to that in PNC with 2 wt%. Thus, PNC might be advantageous for the use in high voltage capacitors and transformers, which operate at high electric fields [17, 20].

2) Breakdown (BD) tests.

Immersed in oil film specimens were placed between a large circular, grounded electrode and a small high voltage one. For dc tests the positive voltage was increased at a rate of 90 V/s, while for ac tests the voltage was increased at a rate of 70 V_{rms}/s until breakdown [16, 18, 21]. Incorporation of clay platelets in PP increased the ac and dc breakdown strength. The effect could be due to the reduction of spherulites size, caused by clay nucleation. Charges could be trapped at the interfaces reducing the probability of breakdown. Taking into account the experimental error, the incorporation of 2 or 4 wt% organoclay increased the BD strength by the same amount. However, while in ac BD increased from 116 for PP to 134 (± 10) kV_{rms}/mm for PNC's; in dc the change was more substantial (from 354 ± 85 to 488 ± 130 kV/mm). Thus incorporation of nanoparticles increased the breakdown strength by 15 and 38% in ac and dc field, respectively.

Bulinski *et al.* studied PP-based PNCs containing 0, 2, 4 and 8 wt% of synthetic organoclay [20, 21]. The other ingredients of these PNCs were the same as listed in Table I and the method of compounding, forming and testing was as described. The synthetic organoclay was the tetrasilicic fluoromica 4CD-Ts from Topy Ind., intercalated with *di*-methyl *di*-stearyl ammonium chloride [4]. The synthetic clay is more hydrophobic, has platelet with large aspect ratio: platelet width/thickness $p < 6000$ and it is free of contaminants.

3) Electroluminescence emission (EL).

EL originates in the space charge injected into the material. PP and PNC comprising 2 and 4 wt% organoclay were tested in ac field in steps from 2 to 24 kV_{rms}/mm, in the photon-counting mode. These tests were paralleled with the dissipation current measurement (DCM). EL was observed only

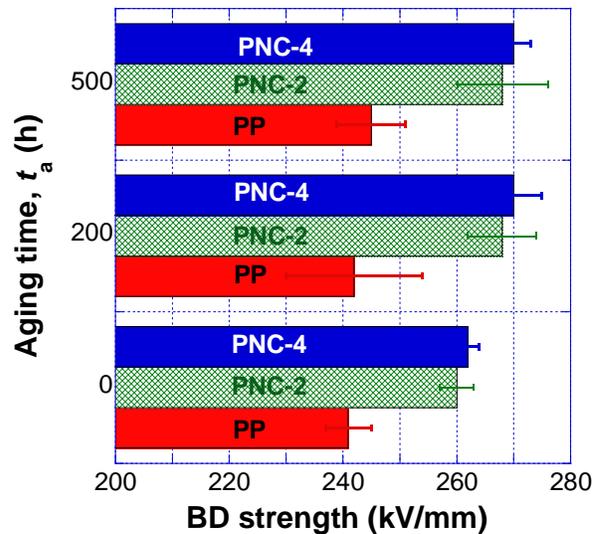


Figure 2. Breakdown strength vs. aging time for PNC with 0, 2 and 4 wt% synthetic organoclay [21].

above 12 kV_{rms}/mm; above this value EL for neat PP increased rapidly, whereas for PNC with 2 and 4 wt% organoclay the increase was much slower and similar for both compositions. Thus, addition of organoclay to PP dramatically reduced the EL change with voltage, for example, while at 24 kV_{rms}/mm the EL for PP was 4.8 kp (thousand pulses) for PNC with 2 and 4 wt% it was 1.6 kp [20].

4) Capacitance and loss measurements.

It is to be expected that conductivity vs. clay content will show a percolation threshold near the clay content where ionic layers of dispersed clay platelets or stacks start overlapping.

Incorporation of 2 and 4 wt% organoclay increased PP capacitance (C_p) by 13 and 19%, respectively. Stronger effect was obtained for the loss tangent ($\tan \delta$) viz. by a factor of 10.7 and 22.8, respectively. It is the presence of polar species (clay, intercalant, and compatibilizer) that so substantially increases the PNC loss factor. For the same reason, the dc conductivity of PNC is higher than that of non-polar PP. However, aging PNC in dc fields increases its dc conductivity far less than that of neat PP.

Schönhals determined the dielectric behaviour of PP-based PNCs with 0, 2 and 6 wt% of organoclay as a function of temperature (T) and frequency (ν) [19]. In accord with the previous observations, the author found that the dielectric loss increases with clay content and so does the permittivity at low frequency. The increase of dielectric loss is caused by increased conductivity and Maxwell/Wagner/Sillars polarization changes with T and ν , due to blocking of charge carriers by clay platelets and their double layers. Addition of organoclay increased the dielectric loss factor over broad frequency and temperature ranges. Again, aging the PNC samples did not significantly change the behavior. Charge trapping at the nano-filler particle/polymer matrix interfaces is the most likely cause.

5) Partial discharge erosion tests.

The partial ac discharge erosion test was performed for up to 6 h at 2 and 5 kV_{rms}, 600 Hz with a tungsten rod electrode [22]. The raw data are shown in Figure 3. The difference in behaviour is striking – while in neat PP the depth linearly increases with time (for up to 40 h) in the presence of clay the erosion shows a plateau. The level of plateau depends on clay content. One expects that at the bottom of the eroded well there is a layer of clay blocking further erosion. For lower concentration one needs to degrade more PNC to reach the erosion blocking clay concentration, thus the well must be deeper. A similar mechanism has been noted for the thermal degradation of PNC [23].

D. Effect of PNC Composition and Preparation on Properties

1) PNC components and composition.

There is a large chemical difference between the polymeric matrix and clay platelets. The polymer of interest is a hydrophobic hydrocarbon, thermodynamically immiscible with the hydrophilic silicate. The two-step compatibilization creates a diffused ionic layer around the clay platelet, with additional ion clusters dispersed in the matrix. The interface between clay and matrix is further complicated by the physico-sorption of organic molecules (e.g., the matrix polymer) and its solidification, increasing the effective solid content (this explains the large increase of modulus and barrier properties caused by addition of small amount of well-dispersed clay). Clay is an efficient nucleating agent that increases the crystallinity. However, depending on the type and amount of intercalant and compatibilizer, these components may shield the clay and prevent nucleation.

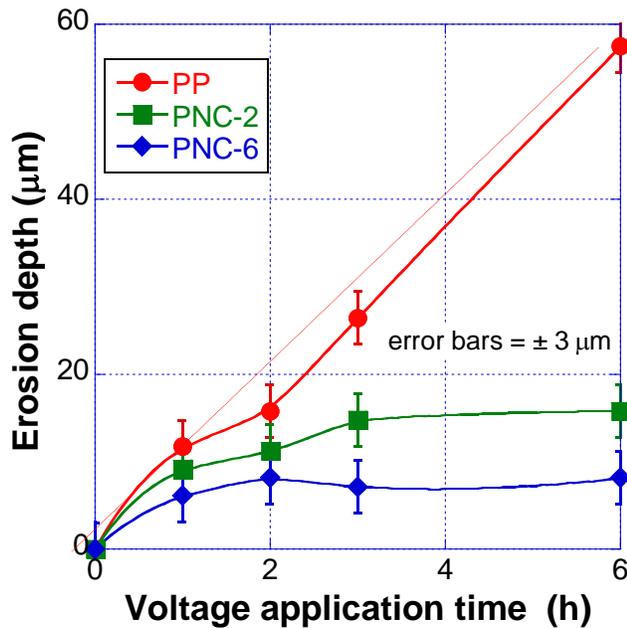


Figure 3. AC erosion depth vs. voltage application time for PNC with 0, 2 and 6 wt% C15A [22].

2) Preparation of PNCs.

Preparation of PNCs is widespread around the world, in laboratories and in plastics industry. The methods of compounding are known. However, they rarely lead to exfoliation in semi-crystalline, hydrophobic matrices such as PP or PE. The specimens used in this study were formed using standard processing equipments in a general pilot plant. The compounding and forming was carried out without special precautions usually taken for the production of high purity dielectric films. However, since such a facility and procedures are known, production of high quality PNC films for dielectric application should not cause problems.

3) Properties of PNCs.

The effects of clay incorporation increase with the degree of clay dispersion. For most commercial clays with aspect ratio of about $p = 280$, full exfoliation of clay platelets is feasible only at low concentration, $w \leq 1.14$ wt% of inorganic clay. Above this limit the crowding of platelets causes them to locally align, forming oriented stacks of decreasing interlayer spacing. The high energy clay surface causes solidification of the organic phase up to 6 nm thick. At about 3.6 wt% of clay the stacks with solidified polymer layer around them will occupy the full space and additional organoclay will remain non-dispersed. Thus, the often cited upper limit of inorganic clay content of 5 wt% is over-optimistic. Most PNC show the best performance within the concentration range of 2 – 4 wt% organoclay, i.e., about 1.2 – 2.4 wt% inorganic content.

Depending on the presence of the contaminating transition metal ions (e.g., Cr, Mn, Fe, Co, Ni), clay may catalytically accelerate degradation. The Wyoming clay is known to contain large quantity of Fe⁺³, which increases the thermal degradation. However, recent studies showed that metal scavengers may eliminate the catalytic activity of clay and stabilize PNC [24]. There is no simple answer regarding the PNC outdoor performance – there is a large variety of clay compositions as well as that of weathering influences. However, clay has a beneficial influence on UV degradation as this process increases clay content in the surface layer, what effectively stops the UV effect. It is noteworthy that clays suppress polymer flammability by limiting access of oxygen through formation of a crust [23, 25, 26].

Incorporation of a small amount of organoclay has large effects on the mechanical and barrier properties, but moderate one on the dielectric behaviour. The brief summary of the electrical and dielectric test results shows the importance of the ionic layer surrounding the nano-particles. By contrast, it seems that the intrinsic properties of the clay platelets (e.g., chemical composition or aspect ratio) have smaller effect on the dielectric behaviour of PNCs.

The discussed PNC samples have been used in the VAMAS- round robin tests (RRT) on the electrical and dielectric properties. The results indicate that addition of organoclay to PP may result in better performance. However, there is large difference in values reported by different laboratories. For this reason it seems more reasonable to compare the relative effect of clay addition determined in a single facility.

Several improvements of dielectric performance have been reported, for example that ac breakdown strength (BD) of PP increased after addition of 6 wt% organoclay from 131 to 160 kV_{rms}/mm. Furthermore, it is noteworthy that **this modest positive effect of nanofiller addition is in sharp contrasts with large negative produced by incorporation of micro-fillers.**

Clay addition caused virtual arrest of PP aging effects in several tests. This was evident in the space charge effects – the accumulated charge in PNCs with 2 wt% organoclay started decreasing after 240 h of aging, while that in PP continued to increase with aging time $t \leq 500$ hrs reaching the charge value 2.5 times larger than that in PNC. Similar effect was observed in dielectric tests and breakdown strength measurements.

The clay effect on the PD erosion is also worth attention. Since the effect seems originating in the formation of concentrated clay layer that stops erosion, even coating the prone to erosion part may offer a simple, economic solution.

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IV. VIEWS AND STATE OF THE KNOWLEDGE

A. On imaging and microstructures

1) Structure and composition.

One of the most pressing difficulties in understanding the properties of nanomaterials, such as nanodielectrics, relates to difficulties in obtaining a complete picture of these materials structure and composition at the nanometer level. This is especially difficult in nanocomposite materials. In such materials, that contain a large number of nanodispersoids, with dimensions from a few nanometers to about 100 nanometers, how can we understand the general macroscopic properties of the materials if we do not have a complete understanding of the nanostructures at the nanometer or even atomic level? It is something to observe or to analyse the general structure, as it can be done through x-ray diffraction for instance; it is quite a different task to observe directly the structural variation at the nanometer level, as it can be done using high resolution transmission electron microscopy (HRTEM). For instance, Figs. 1 and 2 show transmission electron micrographs of a nanodielectrics material composed of silicon oxide crystals (with size varying from μm to nm) as well as nano clays, imbedded in epoxy matrix. One can see in these two micro-

graphs the large amount of different structures with various dimensions down to the nanometer level.

Such high resolution observations are critical for understanding the properties of nanodielectrics. However, in materials where the structure is designed at the nanometer level, with the addition of nanodispersoids, what are even more critical are the properties of grain boundaries. It is well known that as we decrease the average crystalline or structure size in materials, the amount of atoms that found their place at the surfaces of grains increase drastically, especially below 10 nm. For instance, for an average 5-nm grain size, nearly half of the atoms are present at the surface of crystals [1]. Such large amount of atoms present at various interfaces results in materials having most of their properties determine or partly controlled by the properties and composition of these interfaces.

This critical influence of grain boundaries and interfaces has a number of important consequences for nanodielectrics:

- The composition and structure of the grain boundaries need to be known and carefully understood. This means that we need to develop the tools, principally in high resolution transmission microscopy, to probe these boundaries. Today, for some particular crystalline structure, it is possible to identify a single doping atom in a very regular structure [2]; however, direct observation of atoms at boundaries or analysis of chemical variation at interfaces, is a much more difficult proposition.
- The presence of light elements such as hydrogen or other gaseous impurities like oxygen, nitrogen, carbon or sulfur, that diffuse naturally to grain boundaries, can be extremely difficult to observe or control but can have a major influence on the overall properties of nanomaterials.
- Even if such impurities do not have a direct impact on

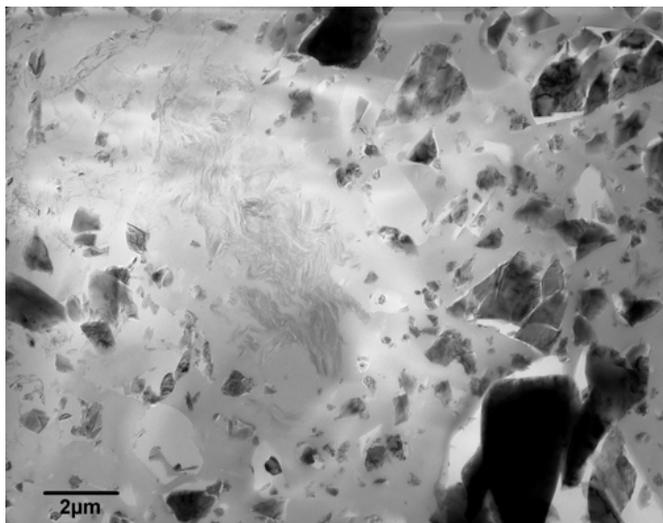


Figure 1. Low resolution transmission electron micrographs of nanocomposite materials showing the components having variable size and structure down to the nanometer level.

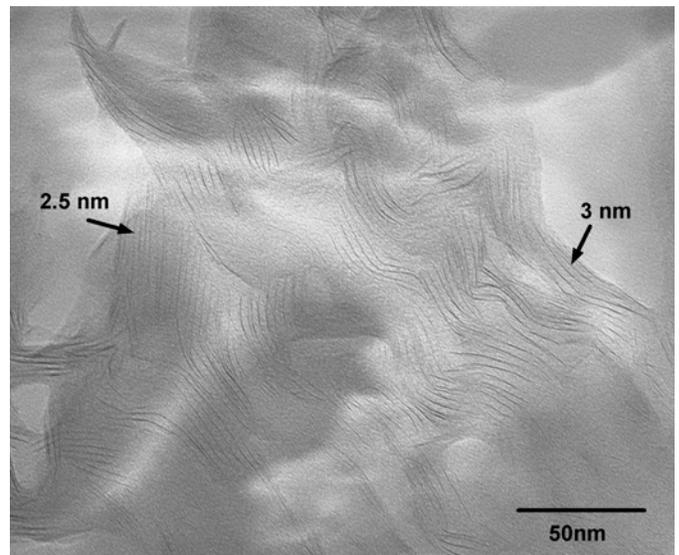


Figure 2. High resolution transmission electron micrographs of nanocomposite materials showing the components having variable size and structure down to the nanometer level.

the property of interest for a particular nanomaterial system, they still can have a crucial impact on other properties, such as formability or life expectancy. Because of this, the synthesis processes of nanomaterials, such as nanodielectrics, need to be extremely well controlled.

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2) Phase morphology.

The goal of this section is to show how to characterize the rate of crystallinity in nanocomposite HDPE/SiO₂ by X-rays diffraction and to compare it with that measured by DSC.

X-ray diffraction (XRD) is a definitive technique for estimating the degree of crystallinity in polymers. Many methods have been devised to calculate the crystallinity of XRD. All other methods require that the intensity due to the amorphous scattering be separated before one begins to evaluate the crystallinity. In this report we discuss how such parameters in X-ray diffraction can be obtained by profile fitting a highly crystalline sample available for that particular nanocomposite, and illustrate this idea by using the data from our materials.

The profiles of peaks could be described by a modified Lorentzian. The XRD patterns of HDPE and its nanocomposites show two distinct (110) and (200) reflection peaks associated with the orthorhombic structure of HDPE. The (110) and the (200) peaks are observed at 25.35° and 28°, respectively. The crystalline peaks of polyethylene can be discerned from the amorphous region by the deconvolution profile fitting. From Fig. 1, some parameters such as full width at half

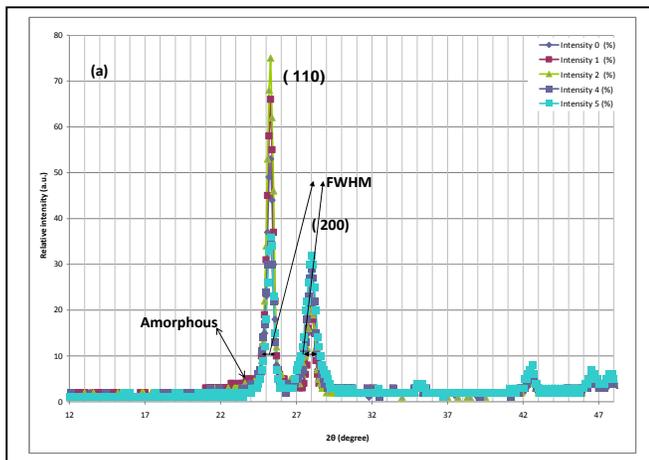


Figure 1. XRD patterns of HDPE/SiO₂, Intensity versus angle diffraction for 0%, 1%, 2%, 4% and 5% nano-SiO₂.

maximum (FWHM) and the degree of crystallinity can be obtained. The FWHM of the polyethylene crystalline peaks, i.e., FWHM (110) and FWHM (200), can be employed to describe the crystallization rate of HDPE/SiO₂ nanocomposites.

Table I shows the crystallinity as a function of load content obtained from the DSC and XRD measurements. It was found that as the content of nanocharges increased, the crystallinity of the nanocomposites also increased. A possible explanation is that the nanoparticles act as an agent of nucleation for the crystal growth.

TABLE I. CRISTALLINITY CALCULATED FROM DSC AND XRD MEASUREMENTS INVOLVING HDPE

Samples	DSC measurements	XRD measurements
0%SiO ₂	55%	52%
1%SiO ₂	61%	59%
2%SiO ₂	64%	60%
4%SiO ₂	69%	66%
5%SiO ₂	72%	68%

B. Do chemical effects take over the nano-effects?

Dispersing nanoparticles into polymers lead to enhancement of thermal and mechanical properties of the composite with respect to the conventional material and it is hoped that similar effects could be observed on electrical performances. Improvement of electrical behaviour has indeed been reported on different types of PNC. Such modifications are attributed, besides to the presence of the filler, to the much higher surface area to volume ratio associated with the presence of nanoparticles with respect to micrometric-size fillers. We would like to emphasize here that it is most of the time highly challenging to relate changes of electrical properties with the nanometric size of the dispersion. This is so mainly because nano-particles dispersion into polymers involves complex preparation steps which can be highly influential on the electrical properties.

The case of one of the oldest polymer based nanocomposite, layered silicate dispersed in polypropylene matrix, which has been characterized in details, is a perfect example. First, starting from isotactic polypropylene, a compatibilization process is needed since the matrix must be rendered polar to enhance PP chains entrance into clay galleries. To achieve this, maleic anhydride (a polar species) is grafted on the PP chain using peroxide; this first step already involves several chemical by-products. The clay is also modified in terms of interlayer distance and organophilic capacity by exchange of intergallery sodium cations by protonated octadecylamine, a process that generates ionic moieties. This complex synthesis route [1] allows controlling the interactions between the host material and nanograins.

What is generally observed is that the PNC properties are different from those of the polymer alone [2, 3]. However, taking into account the complexity of the PNC, it becomes a difficult task to assign a given property evolution to a nano-size effect. All the involved chemical processes are not neutral when dealing with optical and electrical properties of the PNC. For example, it has been shown [3] that the optical properties in silicate PP based NC are mainly controlled by the compatibilization process of the PP matrix and that the active recombination centers are those of the matrix. Space charge behaviour has been shown to depend more on the matrix (isotactic vs. syndiotactic PP) than on the clay concentration. The dielectric losses are increased by the grafting and the clay concentration and this is linked with the ionic species resulting from the manufacturing processes [4].

It is well established that dielectric properties and charge transport is highly sensitive to chemical/physical features of the matrix. Keeping in mind the example of PP based silicate NC, compatibilization and silicates dispersion change both the microstructure of the NC and its chemical nature. Through microstructure, the distribution of energy levels assisting electronic charge transport is changed. Through chemistry, the density and depth of deep trapping centers giving rise to space charge phenomenon are also altered. The presence of ions would also change the electric and dielectric behaviour. This is to say that the attribution of a change in electrical properties to increase of the surface area to volume ratio should be done on the basis of experiments where every step in the preparation of the NCP is under control. This is very demanding from the point of view of material preparation but we believe it is the only way to go forward in the understanding of a specific effect of the increased surface area to volume ratio.

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C. *Blurs of the nano-effect in presence of inorganic oxide nanoparticles in a polymers*

The first successful nanocomposites incorporated nanoscale clay into a polymer host material [1]. The subsequent handling of these composites is well understood but the dielectric properties are difficult to predict, due to the chemistry involved in introducing the clay into the polymer. An alternative to clay are nanoscale inorganic oxides, of which there is a wide range to choose from. Examples are Aluminum oxide (Al_2O_3), aluminum nitride (AlN), boron nitride (BN), magnesium oxide (MgO), silicon dioxide (SiO_2) or titanium dioxide (TiO_2) to name a few. At the zeta potential where their agglomerates become unstable [2], these particles can be dispersed in a solution by means of e.g. ultrasonification and consequently modified with silane coupling agents (SCA) in order to keep them separated [3]. The SCA consists of a hydrolyzable and an organofunctional group, which needs to be chosen according to the used host and filler material. Via the SCA the nanoparticles connect with the polymer host, forming strong bonds. It is agreed upon that the interfacial region between particle and host affects the dielectric properties [4, 5]. However, the exact nature of this interface region is still unclear.

Initial results regarding the permittivity of polymer-based nanocomposites were astounding since they defied conventional wisdom. Introducing a small fraction of nanoscale filler material into a polymer host reduces the relative permittivity. Traditional theories would suggest that a composite of two materials would have a relative permittivity with a value between the values of the constituent elements, instead of being lower than either of them. The reason for this unique behaviour turned out to be an immobilization of polymer chains surrounding the nanoparticles. This effect might very well occur in composites with conventional filler material, which is in the micrometer range, but was not perceived as a pivotal point for dielectrics. Due to the increased importance of the interfaces in nanodielectrics, this effect is of great importance. It leads to an important question: to what extent does the filler material influence our composites? The previously often ignored structural changes on a molecular level are now of high importance, as the aforementioned example illustrates.

The main parameters affecting the properties of a nanocomposite can be identified as follows:

- Filler size, material and aspect ratio
- Surface functionalization
- Fillgrade
- Host material
- Type of synthesis (in-situ, ex-situ, mixing process, polymerization, etc.)

These parameters consequently are reflected in the quality of dispersion of particles within the host material. Until recently the tendency was to assume that the host material does not change due to the introduction of fillers. Now we think that this is not the case and the presence of a filler material does

change the host itself. Polymer chains usually align according to intermolecular forces. The chains that bond to a particle surface via SCA are therefore forced to align according to their neighboring molecules. This leads to a restructuring of the host material due to the presence of the particle and its ability to interact with the host material. Question is now if the presence of the particle and its shape or aspect ratio is more significant than the material the respective particle consists of?

Looking at dielectric spectroscopy results on nanocomposites we notice a trend for the permittivity depending on the filler fraction. The real part of the permittivity is decreasing with decreasing nanoscale filler content, until it reaches a minimum which usually lies at filler contents lower than 2 % by weight or 0.35 % by volume [6, 7]. After this local minimum the permittivity increases, surpassing the value for the base material eventually. Here the properties of the filler material become more dominant compared to the changes in the host material. Where this point lies seems to be dependent on the particle properties (material, surface modification, size and fill grade). It is safe to say that none of the aforementioned influences alone leads to the property changes. It is the combination of all these factors that lead to the results and it is important for engineers dealing with nanocomposites to be aware.

The aspect ratio of the filler material is also of concern. Spherical particles lead to different properties than platelets or rods. Alignment of the filler within the matrix could also lead to differing results. If the filler distribution is random or if it is aligned to form chains throughout the composite, anisotropic behaviour may be the result. Future applications can exploit this anisotropy in various ways.

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D. *Glass transition phenomenology*

1) *The nature of the glass transition.*

The glass transition constitutes an important phenomenon for many classes of materials, in that it is frequently associated with a marked change in physical properties. In the case of

amorphous linear polymers, for example, the glass transition corresponds to a change in modulus of several orders of magnitude, from a brittle solid well below the so-called glass transition temperature (T_g) to a viscoelastic solid or viscous liquid at higher temperatures. However, if mechanical properties are measured under an oscillatory strain, then the resultant marked decrease in modulus described above is seen to occur at a temperature that is dependent upon frequency; a lightly cross-linked rubber may appear elastomeric at 1 Hz but behave as a glassy solid at ultrasonic frequencies. If isochronal measurements of sample volume are made at constant pressure, the glass transition manifests itself as a change in the gradient of a plot of specific volume against temperature. The temperature at which this occurs is, however, dependent upon the length of time at which the specimen is held at each temperature prior to measuring its volume; the longer the time, the lower the apparent T_g .

The physical state of a glass is dependent upon many factors, but it is rarely if ever, in thermodynamic equilibrium. For example, if a polymer is quenched from a temperature T_1 to another temperature T_2 , where $T_1 > T_g > T_2$, then the initial glassy state will depend upon both T_1 and T_2 ; thereafter, it will tend to relax towards thermodynamic equilibrium, a process termed physical ageing. The origin of such effects is well illustrated by the Gibbs-DiMarzio theory, which builds on Flory's earlier work on polymer solutions. Put simply, this envisages a polymer molecule as an array of contiguous cells within a lattice; adding more polymer molecules to the lattice increases the number of occupied cells and reduces the number and sizes of the "holes" between the polymer molecules (that is, the number of unoccupied lattice sites or the free volume of the system decreases). While the above has been stated in terms of adding more molecules to the lattice, equivalent processes occur when a polymer is cooled. At some temperature, the distribution of free volume in the system is such that molecular motion is no longer possible within the time scale of the measurement; free volume is envisaged as being dynamically created and destroyed locally through the cooperative motion of chain segments. Although theory predicts a finite non-zero temperature at which the configurational entropy becomes zero, which would correspond to the thermodynamic T_g , practically, the concept of T_g is best viewed in terms of free volume and molecular mobility. As such, it is dependent upon molar mass, crosslinking, additives, interfaces, etc. For further details on the nature of the glass transition, reference to the excellent overview of McKenna [1] is recommended.

2) *The glass transition in nanocomposites.*

A key feature in the topic of nanocomposites concerns the role of interfaces and, as such, this area has received considerable attention. In his 2004 paper, Lewis [2] considers the fraction of material adjacent to an interface within a nanocomposite and points out that, in the case of an interphase region of thickness 10 nm, this component will dominate for particles less than about 100 nm in diameter. Numerous studies of nanocomposite interfaces have therefore been undertaken. For example, the application of X-ray photoelectron spectroscopy to PMMA/kaolinite [3] revealed an increase of 0.6 eV in the energy of the oxygen 1s orbital, which was ascribed to hydrogen bonding between the carbonyl groups of the polymer and hydroxyl group in the kaolinite sheets. Electron spin resonance

studies of poly(methyl acrylate) (PMA) and synthetic fluoro-mica demonstrated that, in exfoliated systems, the local mobility of PMA chains is reduced due to the interactions with the nanofiller. The thickness of the rigid interface region was estimated to be in the range 5-15 nm [4].

Interactions such as those described above can have a marked influence on material confined near an interface and this is well illustrated by considering the case of ultrathin polymer films, where both the film thickness and specific interactions with any substrate can affect the glass transition. Most results indicate that thickness effects begin to manifest themselves in the range 50–80 nm [5]; in the case of free standing ultrathin films of polystyrene, a large and molar mass dependent decrease in T_g has been observed [6]. In contrast, in the case of poly(methyl methacrylate), much smaller effects have been reported [7] while, for poly(vinyl acetate), no change was seen [8]; in extremely thin films, the disappearance of a glass transition has been reported [9]. Such effects are generally attributed to reduced restrictions on molecular mobility with decreasing thickness. Where the film is supported upon a substrate smaller decreases and even increases in T_g have been reported [9, 10]. Evidently, both geometric and interaction effects are important.

Another area that has attracted considerable attention concerns the behaviour of confinement within pores. In the case of the small molecular system ortho-terphenyl (o-TP), a decrease in T_g has been reported with decreasing pore size [11] as a result of the material in the nanopores being constrained and vitrifying under conditions of constant volume (isochoric conditions); modelling of such systems [12] indicates that this is an intrinsic size effect related to the influence of a negative hydrostatic pressure on glass formation. Replacing the o-TP with a solution of polystyrene in the same solvent has been shown to result in a more complex form of behaviour involving two glass transitions [13], one below and one above the T_g measured for the equivalent bulk system. The lower of these, which decreases with decreasing pore size, relates to the phenomenon described above, while the higher is associated with molecular interactions at the pore surface. A more complex three layer model has also been proposed, based upon dielectric studies of the dynamic properties of low molar mass hydrogen-bonded organic small molecules within porous sol-gel glasses [14]. Dielectric studies of propylene glycol and two poly(propylene glycol)s (PPGs) of different molecular weight confined in controlled pore glasses [15] have revealed a retardation and broadening of the α relaxation process associated with T_g , and the existence of an additional relaxation attributed to the interaction of a few layers (hydrogen bonding effect) of the confined liquid with the surface of the pore. Elsewhere, T_g has been found to vary in a non-monotonic manner [16], where T_g first decreases and then increases as the pore size is reduced, depending upon which of the above effects (intrinsic size or interfacial interactions) dominates. Petychakis et al [17] studied the dielectric properties of fractions of polyisoprene with molar masses spanning the entanglement molar mass within a porous glass. The results indicate that the molecular dynamics are strongly dependent upon the molecular length, weight, pore size and pore surface treatment. Such experimental observations are supported by theory and simulation [18, 19].

In the case of nanocomposites, effects similar to those described are seen. However, since the systems are generally less well defined, quantitative analysis is more problematical. As part of a study of hydrogen bonding in nanocomposites composed of poly(acrylonitrile-co-methylacrylate) and the rod-like nanoclay attapulgite, Yin et al [20] examined the effect of composition on T_g . Although an apparent increase ($\sim 4^\circ\text{C}$) in T_g as inferred from the mechanical loss, was seen in the system containing 1% of the nanofiller, examination of the raw data indicates that no systematic trend exists as the nanofiller composition increases, suggesting that interfacial effects are minimal. Negligible changes in T_g with composition have also been reported for poly(L-lactide)/polyhedral oligomeric silsesquioxanes nanocomposites [21] and a thermoplastic polyurethane/nanoclay system [22]. In another study of PU-based systems [23], a range of complementary techniques were used to study the glass transition in nanocomposites based upon montmorillonite (MMT). Agreement between the various techniques was found to be good and suggested that similar molecular dynamics occur in both the pure matrix and the nanocomposites. However, evidence also exists for a fraction of the polymer in each nanocomposite that makes no contribution to the glass transition. Evidence for an immobilized interfacial phase that did not affect T_g has also been seen in polyamide/layered silicates systems [24]. Conversely, a study of the mechanical relaxation behaviour of poly(vinyl alcohol)(PVA)/silica nanocomposites revealed two relaxations, which the authors attributed to the glass transition of the PVA matrix (43°C) and segments for PVA chains confined by the surface of silica nanoparticles (83°C). This study went on to deduce that the thickness of the interfacial immobilized was 5–10 nm and dependent upon composition [25]. In the case of polyimide/ ReO_2 nanocomposites, addition of the nanoparticles resulted in a pronounced reduction ($\sim 10^\circ\text{C}$) in T_g [26]; similar effects are discussed by Crosby and Lee [27] in their review on the mechanical behaviour of nanocomposites in connection with molecular confinement. The effect of adding silica nanoparticles of different sizes to an epoxy resin was reported by Ou and Shiu [28]. This work revealed a pronounced increase in T_g (up to 20°C) on adding as little as 0.3% of the nanoparticles; the smaller the nanoparticles, the greater the elevation in T_g . Similar pronounced increases in T_g have been reported elsewhere for both silica and titania-based nanocomposites [29]. However, Singha and Thomas [30] report that the addition of even small concentrations of spherical nanoparticles, (titania, alumina and ZnO), has entirely the contrary result. In this study, a decrease in T_g of some 8°C was reported on adding just 0.5% of nanofiller. Work on epoxy/carbon nanotube systems presents evidence that such effects are not only related to physical effects (surface interactions and confinement) but can also be a consequence of changes in the chemistry of the system. Miyagawa et al [31] investigated the mechanical relaxation behaviour of epoxy/functionalised single-wall carbon nanotube (FSMCNT) nanocomposites and report that the addition of 0.20 wt% nanofiller resulted in a decrease in T_g of $\sim 30^\circ\text{C}$. Thermogravimetric analysis (TGA) of these systems revealed a reduction in the onset of thermal decomposition, an observation interpreted in terms of reduced crosslinking of the matrix, despite the fact that the stoichiometry was unchanged from that used in ideally cured neat epoxy.

Furthermore, modification of the anhydride content was subsequently used to redress this effect. In short, incorporation of nanofiller can affect the cure reaction, necessitating a reconsideration of the optimum matrix composition. Elsewhere [32], the addition of a functionalised MMT to an epoxy resin was shown to accelerate the curing reaction; in this case the observed decrease in T_g was ascribed to alkylammonium cations from the clay acting as a plasticizer.

To conclude, both geometrical and interaction effects can influence free volume and molecular mobility and, consequently, T_g . In the case of thin films and nanoporous systems, the effects seen experimentally have been subject to considerable theoretical analysis and are reasonably well understood. In the case of nanocomposites, equivalent processes should operate. However, even in nominally equivalent systems, contradictory trends have been reported suggesting that either subtle unidentified effects are dominating or, more likely, that issues associated with the reproducible sample preparation and detailed characterisation need to be addressed.

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E. Dielectric response

The dielectric response of loaded insulating materials, whether by conductive or non-conductive particles, has been studied since decades for micrometric loading [1, 2] and more recently for nanosize fillers in either polyethylene, polypropylene or epoxy matrix [see 3-5 for example]. Before tackling the particular case of nanofillers, it might be appropriate to summarize what is generally found for classic micrometric composites. Most of the dielectric data provided in the literature for non-conductive fillers, such as metallic oxides, in a non-conductive polymeric matrix, will feature, in addition to the relaxation mechanisms proper to each phase, an interfacial polarization peak, known as Maxwell-Wagner-Sillars polarization, and an increase of both the real and in imaginary parts of the complex permittivity as the frequency is lowered. Figure 1 shows a typical result for SiC loaded epoxy. The increase of both real and imaginary part of the complex permittivity is related to non-ohmic charge transport, leading to various forms of electrode polarization or the so-called low frequency dispersion [2, 6]

Another universal observation for ordinary composites is that none of the existing mixing laws [1, 2] can fit the experimental data on a broad range of frequencies [7, 8]. Indeed, none of the numerous existing models can even come close to fit the data depicted in Figure 1. For hydrophilic fillers, the

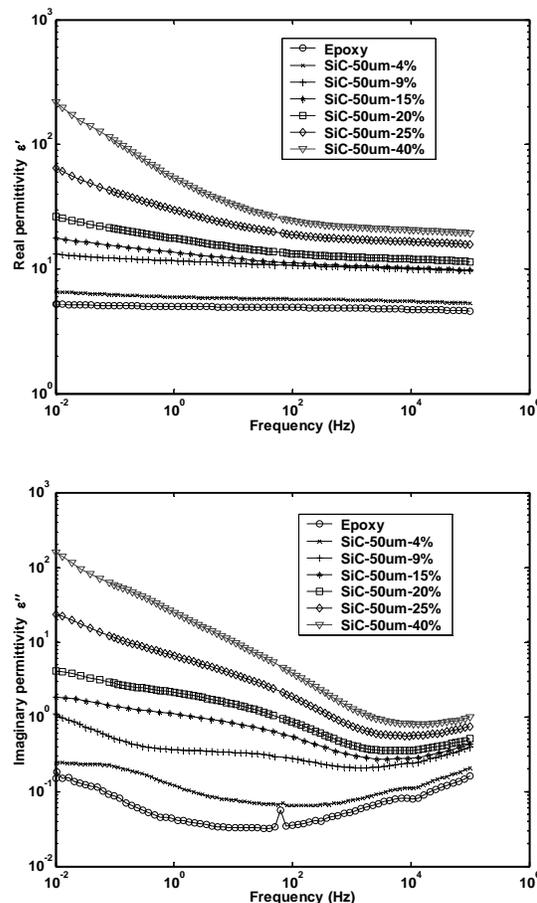


Figure 1. Real (a) and imaginary (b) part of the complex permittivity of epoxy/SiC_p – 50 μm composite as function of frequency (from [7]).

existence of absorbed water in materials and particularly in the interfacial region between the filler and the polymer matrix is almost inevitable and will invariably affect the composite dielectric response, often leading to an interfacial relaxation peak at much higher frequency than what would be expected based on values of the filler bulk conductivity. This effect is expected to be even more pronounced for nanocomposites as the volume fraction of interfaces is much higher. Specific findings related to the dielectric response of nanocomposites are the suppression of the interfacial relaxation peak that is sometimes observed and the decreased permittivity for low filler concentration [4]. A similar effect to this observation can be found in very common materials such as salty water for which the static permittivity reduces as a function of salinity for low salt concentration because all the water molecules that are in the vicinity of an ion orient themselves with respect to the ion [9].

Figure 2 shows the dielectric response of a 5% wt. nanosilica filled HDPE. Details about sample preparation and processing are given elsewhere [10]. In order to fit the data with the Maxwell-Wagner equation (particular case of the MWS equation for spherical particles, see equation 13.5 of [2]), one must use unrealistically high values of conductivity for silica. This fitting is shown in Figure 2 using

$$\epsilon_f^* = \epsilon_f - i \frac{\sigma}{\epsilon_0 \omega} \quad (1)$$

and the experimental data for the neat HDPE for ϵ_m^* (for HDPE, ϵ'' is very low and ϵ' is almost constant for the whole frequency range). To take into account the possible presence of a water interlayer between the nanofiller and the matrix, a three phase model known as the interlayer model [11] can be used. This would justify the position of the relaxation peak shown in Figure 2 but not its shape since this model also leads to a Debye-type relaxation process. A possible explanation for the shape of the relaxation peak is a distribution of the interlayer conductivity. This would be in good agreement with the microscopic examinations of the composite shown in Figure 2 that revealed a somewhat broad distribution of the inclusion sizes [10]. This suggests that dielectric spectroscopy is a good tool to assess the quality of the particle distribution.

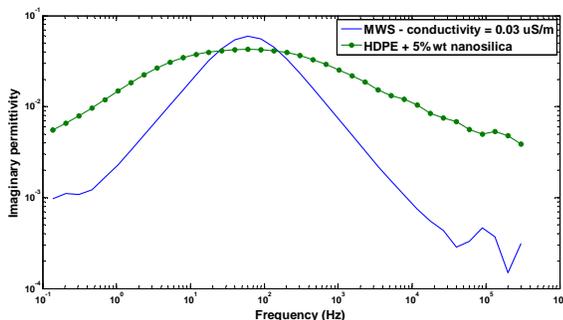


Fig. 2: Imaginary part of the complex permittivity of HDPE loaded with 5% wt. (volume fraction = 0.02) of nano silica compared with the MWS model for spherical particles with a conductivity of 0.03 $\mu\text{S/m}$.

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F. Space charge and ageing involving nanocomposites

1) Space charge formation.

Does the addition of nanoparticles in an insulating matrix affect significantly the space charge accumulation? To try to give some answers to this question, we have analysed a micro-composite epoxy (micrometric silica dispersed in an epoxy matrix at a loading of 60% by weight) and the same material with nanofiller (adjunction of a small amount of nanoclays 0,45% of the total weight). The space charge accumulation has been obtained by using the Thermal Step Method (TSM) with variation of electrical and thermal ageing duration times (up to 1611 hours under 15 kV/mm at 60°C) [1]). The TSM is a non-destructive technique allowing to follow up the evolution of the space charge accumulation in time.

Figure 1 exhibits several significant results:

- The nanofilled sample seems to accumulate less space charges throughout the ageing;
- After 400 hours, the space charge accumulation seems to decrease in the nanofilled;
- The sample without nanofiller presents stronger oscillations on the total trapped charge;

The last point could be explained by considering that the sample must reach a significant level of local electric field before discharging. In presence of the nanofiller, the flow of charges

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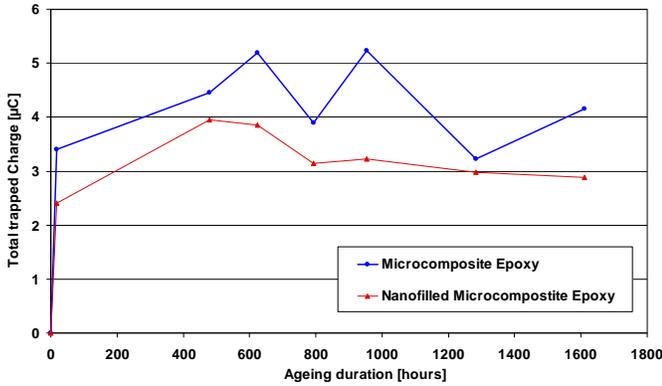


Figure 1. Evolution in time of the total trapped charge corresponding to the sum of the value of the positive trapped charge and the absolute value the negative trapped charge versus the applied electric field.

starts for the lowest remnant electric field levels. This could probably be due to the presence of particular volumic conduction phenomena as if nanoparticles feature a “localized bridge effect” role. Finally, the observed strong oscillations over time (seen on the figure) could result in the long term by a premature ageing of the material without nanofiller while the nanofilled sample tends to stabilized vs. ageing duration.

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2) Nanocomposite ageing.

One of the main goals of adding inorganic nanofillers to a polymer matrix is the improvement of electrical performance of the nanocomposite material. In particular, longer life in service can be expected by increasing electric strength and endurance. Nanofiller type, size and density have to be tuned properly on the basis of the specific properties which have to be improved [1, 2]. Moreover, these properties are correlated to the application in which such materials will be used. For instance, under ac supply resistance to partial discharge (PD) activity is an important property which can increase remarkably material life in service [3, 4]. Under dc conditions, on the contrary, PD resistance has not the same importance as space charge accumulation, which is known to have to be reduced in order to guarantee long insulation life [5, 6].

For this purpose, the following experiments were performed on flat specimens with and without nanofiller:

- 1) Ac life tests under PD activity in needle-plane cell at 10 kV (5 times the PD inception voltage). Tests were performed at 250 Hz in order to reduce test times. Specimens of base epoxy resin (N0) and containing 5%wt (N5), 10%wt (N10) and 25%wt (N25) of silica nanofiller were aged until breakdown. Surface erosion was also measured at fixed time intervals [4].
- 2) Space charge measurements were performed at different fields on base polypropylene (PP) specimens and with 5% layered silicates (LS). A polarization phase of

Table I: Failure times (scale parameter of the Weibull distribution) and relevant confidence intervals for the tested materials.

Material	Failure time [h]	90% Confidence Interval [h]
N0	180	±31
N5	360	±52
N10	1280	±176
N25	2750	±224

10000s was followed by depolarization which lasted 3600s. The maximum stored charge density at the beginning of depolarization is measured [6]. Ac and dc electric strength tests were also performed on these specimens.

Failure times, namely the scale parameter α (63.2th-percentile) of the Weibull distribution, obtained from ac aging tests under PD activity performed on each material are reported in Table I, together with the relevant confidence intervals at 90% probability. As expected, nanostructured materials withstand better PD erosion with respect to the base epoxy. Moreover, increasing filler content life performance improves largely. Failure time for N25 is, in fact, almost one order of magnitude larger than for N0 and N5. This is confirmed also by erosion area measurements reported in Fig. 1. Material N25 shows, in fact, a much slower increase of surface degradation with respect to the other materials. Under dc conditions space charge accumulation is shown to be significantly reduced by the nanofiller presence. Figure 2 reports the max absolute stored charge density, q_{max} , accumulated in the material as a function of poling field. It can be observed that, although the threshold field for space charge accumulation is reduced for the nanofilled materials with respect to the base material, i.e. from 14 kV/mm to 5 kV/mm, the former accumulates less charge than the latter at fields larger than 30 kV/mm. These

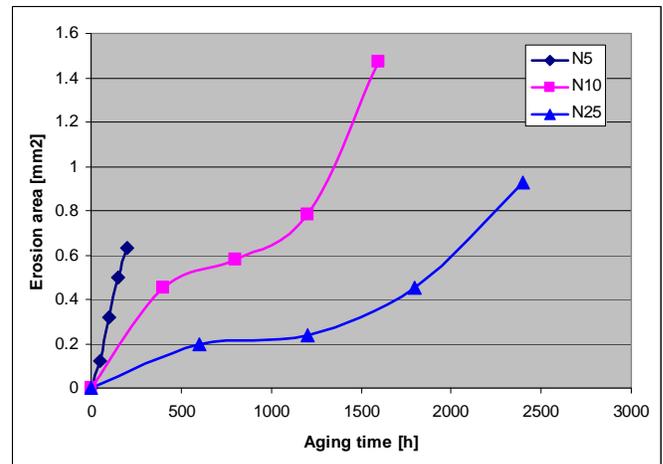


Figure 1. Erosion area as a function of aging time for the nanofilled tested materials.

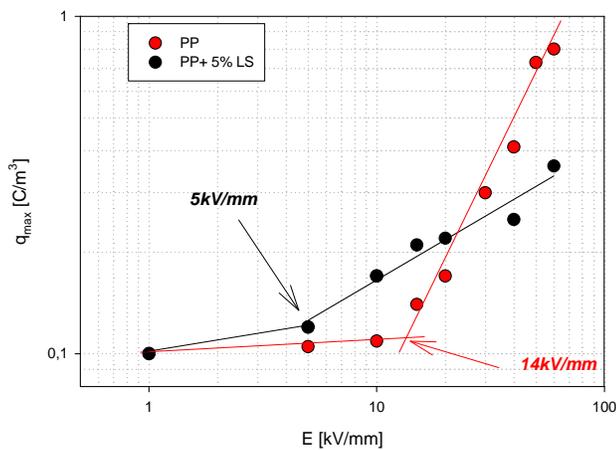


Figure 2. Maximum stored charge density q_{max} , as a function of poling field for PP and PP + 5% layered silicates (LS). The arrows indicates the thresholds for space charge accumulation.

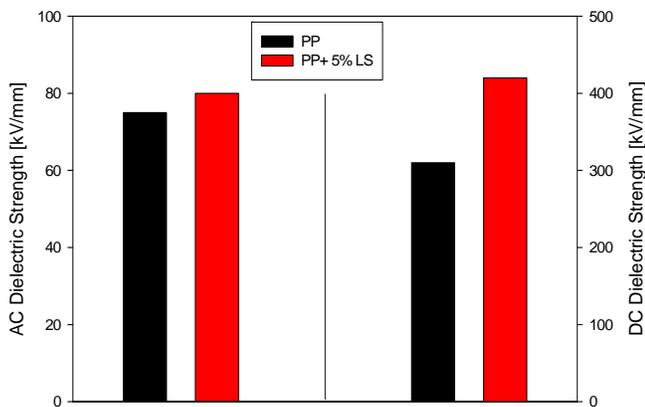


Figure 3. Ac and dc electric strength for PP and PP + 5% layered silicates (LS) specimens.

results indicate that a relatively small percentage of nanofiller is able to modify significantly space charge trapping features of the base polymer, e.g. increasing charge injection barrier and/or acting as shallow trap for charges.

The better space charge performance of the material leads to improved withstanding of dc field for the nanofilled material, as shown by the increase in the dc electric strength in Fig. 3 (note that under ac electric strength of base and nanofilled material is similar).

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G. On the erosion performance

Though during recent years numerous original publications and review papers have been devoted to nanodielectrics, information concerning their resistance to erosion caused by different types of electric surface discharges is still scarce. Among the types of the surface discharges evaluated, corona, partial discharges, gliding discharges and arcing dominate. All these discharge types have detrimental impact on material performance and it has been of vital importance to investigate how much the use of nano-fillers may improve the performance and reliability of insulation systems.

When tracing a few years back, Lei and Xishan [1] reported first on the resistance to tracking and erosion of room temperature vulcanized silicone rubber (RTV) coatings filled with nano-silica and nano-layered silicate. The authors concluded that flame suppression mechanisms of the nano-filled composites were absolutely different from that of ATH filled RTV and the sphere and layered shaped nano-filler particles could take over the role of flame retardant. Later on, Lei et al [2] extended the work to investigations of the materials to corona discharges and proved that nano-filled RTV performed better than traditional RTV. It was also shown that nano-layered silicate filler could be dispersed in the SIR matrix uniformly and with only 5 wt% concentration contributed to improved tracking resistance and mechanical properties [3].

El-Hag et al [4] demonstrated that performance of silicone rubber (SIR) filled with 10 wt% of fumed nano-silica was similar to that of 50 wt% micro-filled one. The authors also applied laser ablation technique to evaluate the erosion performance of the samples [5] and postulated that formation of silica like layer helped to impede the degradation of SIR in the nano-filled material, which resulted from the strong bonding between nano-filler particles with the rubber matrix. Despite of the differences in erosion resistance, the investigations revealed that both nano- and micro-silica filled SIR retained similar thermal conductivity. The nano-silica filled RTV was also suggested to be better suitable for use in contaminated environments since it had a higher erosion resistance [6].

In parallel, Rätzke and Kindersberger [7] evaluated the effects of silica and alumina nano-fillers on the resistance to arcing of silicone SIR elastomers. The authors demonstrated a longer test time withstand with increased filler concentration and pointed to the importance of a good filler dispersion. The necessary good dispersion could only be achieved in case of nano-silica, while alumina nano-filler agglomerated and rather acted as ordinary micro-filler. However, the enhanced resistance to arcing became only evident with relatively high concentration (~40 wt%) of the silica nano-filler. Further investiga-

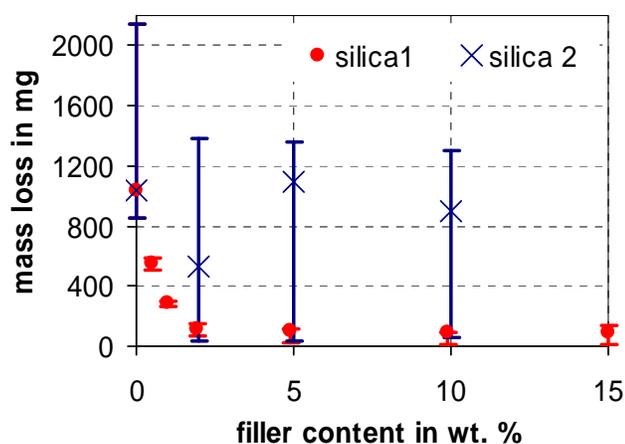


Figure 1. Median, maximum and minimum values of the mass loss occurring during the tracking and erosion test (according to IEC 60587) of a silicone matrix material with two different silica filler materials for three samples each.

tions were done using a silicone rubber with a precipitated (silica 1) and a fumed (silica 2) silica nano-filler (~40 wt%) of the silica nano-filler. Further investigations were done using a silicone rubber with a precipitated (silica 1) and a fumed (silica 2) silica nano-filler [8-9]. Both filler types were untreated and hydrophilic. The results showed a highly improved resistance to high voltage arcing and resistance to tracking and erosion (**Erreur ! Source du renvoi introuvable.**) already at low filler contents (< 5 wt%) of the precipitated silica compared to the silicone rubber without fillers.

For the materials with fumed silica no significant improvement was observed. The different behaviour was explained by the estimated interphase content, which seems to be high for strong interactions between filler and matrix material and small for weaker interactions. This assumption was supported by TGA measurements [9]. Also Venkatesulu and Thomas [10] showed that the performance of a composite filled with 4 wt% nano-particles was comparable to that filled with 30 wt% microparticles.

Investigations on possible improvements in nano-filler dispersion and its effect on tracking resistance were recently performed by Ramirez et al [11-13], who modified nano-filler particles with surfactants and showed that one of them, e.g. TritonTM X-100, appeared especially suitable for improving the dispersal and therefore resistance to arcing and to heat erosion in silica and alumina based SIR compositions.

Epoxy based materials with surfaces structured with nano-particles and characterized by superhydrophobic properties (contact angle $\geq 130^\circ$) were recently evaluated by Wu and Schnettler [14] for their performance in modified rotating wheel dip test, clean fog test and condensation test. While the performance became enhanced under rain or fog conditions, a decline in the resistance to form continuous moisture layer was observed under dew condition. Also bulk filled epoxy composites, containing nano- and micro silica fillers, were also recently evaluated within CIGRE WG D1.24. Changes imposed by corona and ozone treatment on electrical properties (surface and volume charging currents and dielectric response) were investigated by Bin et al [15], who found that the contents of

the micro- and nano-fillers played a significant role in the observed surface changes. Long-term corona-ozone exposure had obvious effect on the surface properties. On the other hand, the effects of the treatment on the volume properties, dielectric permittivity and dissipation factor (dielectric losses) did not exhibit high sensitivity.

The above described investigations had revealed that use of nano-composites may yield satisfying performance under the action of surface electrical discharges. For practical applications, the main challenging questions to be answered in the future concern the possibility of manufacturing large volumes of well dispersed nano-filled materials. At the same time, as the erosion and tracking in electric power applications refer mainly to material surfaces, possibilities to reproduce self-organizing nanostructures that can provide special properties on large surfaces of polymeric materials should be in focus.

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V. THE INTERFACE AND ITS ROLE IN VIEW OF HIGH-DEGREE SELF-ASSEMBLY NANODIELECTRICS

A. *The interface.*

A recent review of the chemistry and physics of the interface of nanodielectrics made using either spherical inorganic nanoparticles or intercalated and exfoliated layered inorganic natural and synthetic clays and micas, by Reed [1], highlights the progress in understanding the role of the interface, but also cites many instances of apparent contradictory results by different investigators, in properties where the measurements are typically repeatable, unlike electrical breakdown. This obtains for samples freshly prepared, and does not include any electrical, mechanical, physical or thermal aging effects.

The fact that there are these differences is not a problem but it emphasizes that there is a lot of interface chemistry involved in making nanocomposites, requiring careful control of each synthesis step; and helps to explain why significantly different performance may result, ranging from indifferent performance relative to the base polymer, to significant improvements in performance in such properties as long term voltage endurance and PD resistance.

Measurements on polymer nanodielectrics of glass transition temperature, free volume, broadband (10^{-2} Hz to 1 GHz) dielectric measurements of the real and imaginary components of permittivity, morphology and infrared and electron paramagnetic resonance (EPR) measurements, illustrate the variations that researchers have found [1], and the difficulty of modeling the interface at this point in time. The glass transition temperature (T_g) provides a good example of this, and of the need to continue confirming results with considerable care in the synthesis, purification, and preparation of samples for testing; and the characterization thereof.

Alcoutlabi and McKenna [2] performed a topical review of 406 theoretical and experimental publications on the effect of nanoparticles on melting point and glass transition temperature. They presented dynamic, thermodynamic, and pseudo-thermodynamic measurements reported for T_g in confined geometries for both small molecules in nanopores and for ultrathin films. They found that T_g increases, decreases, remains unchanged, or even disappears, depending on details of the experimental conditions or molecular simulation. For the same material, depending on experimental conditions, different values of T_g had been observed; it was also noted that the vast majority of the experiments had been carried out carefully and the results were reproducible. The authors conclude that existing theories of T_g are unable to explain the range of behaviours at the nanometric size scale.

On the other hand, Bendler and colleagues [3] have a more positive view, and present a quantitative analysis that shows that most if not all, experimental results on the nanoconfinement of the glass transition temperature can be explained by a defect diffusion model. Their model incorporates defect-defect interaction enthalpy, defect concentrations, defect lattice geometry correlation length, and percolation fraction, to determine T_g ; and provides a quantitative relationship between the percolation fraction of rigid to mobile regions and T_g .

Work by Singha and Thomas [4,5] for different spherical inorganic nanoparticles in bisphenol-A epoxy, as a function of filler concentration, illustrates a strong, unusual sensitivity of T_g to concentration. T_g drops sharply as the concentration increases to 0.5%, then steadily increases as the concentration was increased to 20%. The ability to understand and physically describe this behaviour will be important in improving our understanding of the nano interface and developing a model that can be related to other physical and as-yet-unexplained electrical properties.

The electrical structure of the interface has been represented by Lewis [6] as a Gouy-Chapman diffuse double layer and by Tanaka and colleagues [7] as a 4-layer structure, before the matrix polymer properties are resumed. However, while these models may apply in some cases, their verification has not been confirmed, and in many cases, some of which feature dramatic improvements in properties, the evidence points to a simple non-polar, low conductivity bonding of nanoparticles to the surrounding polymer matrix.

However, as covered in reference 1, there are also some differences in interface characteristics which can be related to the chemical nature of the nanoparticle surface and to the type of polymer matrix (e.g. amorphous or semi-crystalline thermoplastic polymer, cross-linked polymer, thermoset polymer), and to molecular weight and stereo-regularity qualities.

The influence of water on properties such as broadband dielectric or infrared measurements, or low- or high-field electrical measurements, or short- and long-term hydrolysis at the nanoparticle surface and other aging effects, cannot be over emphasized; whether from residual water on nominally “dried” particle surfaces, or water that diffuses into a sample after preparation, or from water/other solvents used in making intercalated/exfoliated polymer nanocomposites. The range of such potentially dominant effects due to water is covered in two recent reviews by Reed [1] and, dealing primarily with the impact of water during the processing of intercalated and exfoliated nanocomposites and the subsequent undesirable effect upon properties, by Bellucci and colleagues [8].

In summary, our understanding and control of the interface is still largely incomplete, and controlled experiments, including the use of tagging agents such as those used by Jeschke [9] in EPR experiments, will help toward improving our understanding.

B. *Self-assembly.*

In contrast with a significant volume of work on nanodielectrics over the past decade and the focused interest in the role of the interface, the insulation and dielectrics literature has shown little evidence that self-assembly has been widely addressed for dielectric polymer nanocomposites.

A summary of the status of self-assembly in dielectric nanocomposites by Reed in 2007 [10] contrasted the prospects with spherical inorganic nano particles, where partial self-assembly has been successfully used, and with intercalated and exfoliated nanocomposites from layered clays and micas. In the latter, multiple processing steps are employed, and self-assembly generally would appear to be ignored, or for proprie-

tary reasons has not been disclosed. Never-the-less, clearly, some of the processing steps are amenable to self-assembly and may likely be desirable in order to achieve improved consistency of the final product and faster overall processing.

An interesting paper which addresses the problem of achieving self-assembly in a 3-D material is that of Sandhage and colleagues [11].

Overall, there has been little published progress with the self-assembly of polymer nanocomposites for dielectric and hv insulation over the past few years; and nothing where details have been spelled out.

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VI. NEW THREATS AT THE HORIZON?

A. Health and safety issues related to nanoparticles

The use of nanoparticles in industrial products is steadily increasing. At the same time concerns about adverse effects of the nanoparticles on human health have emerged [1,2]. These concerns have originated from long-term studies of very-fine air-borne industrial pollution and from the use of asbestos in industrial products [3-7]. The present text provides basic information on possible effects of nanoparticles on human health, safe working practices in laboratories and at industrial working places, and risk assessment of nanoparticles so that

informed decisions about future production lines, the use and recycling of nanomaterials can be made. It should be noted that nanotoxicology is a new field and detailed mechanisms of nanoparticle effects on environment are not fully understood.

Although mankind was always exposed to nanoparticles from natural sources such as volcano outbursts and forest fires, the systematic exposure of humans to man-made nanoparticles started with the invention of fire. With first industrial achievements came also first reports on susceptibility of human health to fine dust and sub-micro sized particles. These reports date as back as two thousand years ago to stone crushers in quarries, workers in coal mines and welders exposed to metallic fumes. Households are no exception when it comes to generation of nanoparticles. Pure wax candles can release 250 000 nanosized particles per cubic centimetre during one evening. Smoke released by one cigar can contain more than 70 000 nanosized particles per cubic centimetre [8]. A recent study has shown that some laser printers release nano-particles [9]. Nanoparticles are also used in the food and cosmetics industry to improve, e.g., the processibility or appearance of a product.

B. Hazard and Risk Associated with the Use of Nanoparticles

Generally there are three ways of human exposure to nanoparticles: skin penetration, inhalation and digestion.

Theoretically skin can be penetrated intercellularly, transcellularly and along the hair shaft. Fortunately skin is relatively thick, consists of several layers and is shed regularly and thus penetration by ordinary (not coated with biologically compatible agents) nanoparticles is less likely [10]. There are many uncertainties though. For example it is not clear whether nanoparticles could penetrate through wounds and cuts. In some skin conditions the thickness of skin can be significantly reduced and thus risk of penetration by nanoparticles is increased. It is also difficult to assess what happens to nanoparticles deposited on skin surface by application of sunscreen containing nanoparticles during physiotherapeutic massage when the nanoparticles might pierce the skin.

There are two possible ways for nanoparticles to enter human body during inhalation. The first path, through nasal cavity and along the olfactory nerve leads directly to brain [11]. This has been confirmed in inhalation studies of carbon nanoparticles in rats. The second path, via alveolar-capillary barrier in lungs allows penetration of nanoparticles into the blood stream and human body natural filters – liver and spleen [12, 13]. It should be realized that human lungs have more than two thousands kilometres of airways and area of about 150 m². Penetration sites for nanoparticles are thus plentiful. Since females have thinner airways than males different deposition rates are expected for males, females and children [14].

During inhalation of nanoparticles part of them will be deposited in the mouth cavity and will end up in the digestion system with food. Once in the digestion system, nanoparticles can penetrate through gastrointestinal barrier into the blood stream and end up in liver and spleen [15]. Nanoparticles from over-worn porcelain bridges were observed in liver of patients [16]. The critical point in these studies was that non-toxic ma-

terials (porcelain) caused health problems and even death. Patients suffering from inflammatory bowel diseases such as Crohn's disease have abnormal intestinal permeability which may allow for easy penetration of nanoparticles.

In general, the smaller the nanoparticles, the further is the translocation in human body and once in human body nanoparticles mostly create damage by generating oxidative species which cause oxidation of human body.

The effect of nanoparticles on environment was examined in several studies. For example, it was observed that Al_2O_3 nanoparticles inhibited root growth in plants [17]. Fullerenes in sub-lethal concentrations changed behavioural patterns of *Daphnia* which in turn increased risk of predation and increased reproductive decline [18]. It was observed that sub-lethal doses of fullerenes led to bio-accumulation in *Daphnia* with lethal consequences. Several types of nanoparticles (MgO , TiO_2 , fullerenes and most notably Ag) were found to be bactericidal [19,20]. The concerns of wastewater treatment plants related to penalties for release of toxic waste harmful to aquatic organisms led to regulation of antibacterial nanosilver in the USA with re-call of products such as washing machines or clothes using or containing nanosilver. Further claims were that nanosilver is highly toxic even in low concentrations and it accumulates in clams. There are several hypotheses to explain antibacterial working of nanoparticles. Since bacteria and spores are usually negatively charged due to presence of carboxyl groups, they are electro-statically attracted to positively charged nanoparticles. Since many types of nanoparticles have sharp edges these by a simple act of abrasion cut through the walls of bacteria and thus physically destroy them [19].

It should be born in mind that most of the toxicological studies focused on a single type of nanoparticles. It is likely that in natural environment, with many types of nanoparticles present, various synergy effects will take place.

C. *Safety measures and risk assessment related to nanoparticles in power industry*

Four areas of human exposure to nanoparticles have to be addressed when adopting safety measures in power engineering industry: 1) production of power equipment. It is preferred to work with liquid suspensions, pastes or granules rather than dry powders, and closed rather than opened manufacturing systems should be used. 2) storage and transportation. The most common danger present spills, vapour leaks and fire during accidents. 3) operation of equipment. Nanoparticles can be released into environment via mechanical abrasion, ablation (surface discharges, flashovers) or from equipment fires. 4) end of equipment lifetime. Ecotoxicity of nanoparticles and sudden catalytic reaction with risk of explosion in incinerators have to be considered during recycling and waste disposal of power equipment. Preparation of ionic solutions instead of solid nanoparticles and creation of microagglomerates may address these challenges.

It should be borne in mind that toxicity of materials depends on the magnitude and duration of exposure. Manufac-

turers of toxic materials follow several basic rules which can also be used for work with nanoparticles and nanomaterials. These are: minimize the number of people working with nanoparticles, minimize the time spent in environment with nanoparticles, maximize protection (wear nano-proof certified clothes and masks, use glove boxes), perform a toxicology study for a given nanomaterial.

It is important to prevent formation of dust and aerosols in the workplace. A small under-pressure in the working area is recommended to prevent escape of nanoparticles to other working areas. Ventilation systems are to be equipped with nanocertified filters to prevent outflow of nanoparticles to nature. Cleaning of the working place should be performed by mopping up or extraction systems but never with blowers.

In absence of clear rules some manufacturers perform measurements of nanoparticles in the ambient air in their facilities on a voluntary base. These measurements are usually carried out by certified health and safety authorities. It is important to realize that the number of nanoparticles in air may vary with the time of nanoparticle production and location in a factory.

Toxicology studies are usually expensive (up to a few millions of USD) and take several years but this cost is insignificant compared with the penalties paid by companies in asbestos victims trials where it was usual to pay several hundred millions USD per company. A typical toxicological study should include [21]: 1) detailed particle characterization. This usually means measurements of spatially resolved chemical composition (coating, bulk), size distribution, agglomeration state with statement on desagglomeration tendencies, shape (spherical, irregular, rods, sharp edges), crystal structure, surface area, surface chemistry, surface charge, porosity, fibre flexibility, solubility, biopersistence, protein adsorption, and many others. 2) exposure to at least three doses. Long-term low-level exposure experiments are important because of possible accumulation of nanoparticles in human body. 3) data interpretation against mass, surface area and number of nanoparticles. 4) nano versus micro control study. Independent toxicological institutes should perform such studies.

Since the field of nanotoxicology is relatively new and regulation is either entirely lacking or is in preparation there is a risk that small companies which lack human and financial resources would introduce products harmful to humans and ecosystem to financially benefit from the present lack of regulation without long term legal consequences [22]. Introduction of basic rules from the health and safety authorities is therefore necessary.

Although the field of risk assessment related to short- and long-term human and environment exposure to nanoparticles is new, the awareness and first steps towards responsible use of nanoparticles has been made by governmental and also non-governmental organizations [23-28].

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VII. MORE ASSETS YET NOT A PANACEA!

So is nanotechnology going to be seen as the universal panacea of the ills of electrical insulation bestowing on it an infinite lifetime? Well probably not but, even considering that workers are more likely to publish "good" results than "bad", the results so far seem overwhelmingly positive. A reasonably wide range of properties covering electrical, mechanical, thermal and chemical characteristics have been reported, often comparing a conventional insulating material with and without "nanoparticles", and sometime one containing "microparticles". An example of the latter is epoxy resin containing silica particles in the range 1 to 100 μm , a formulation that is commonly used in low and medium voltage switchgear for example.

A. Electrical Breakdown Strength

Perhaps the most important property of an insulator is its breakdown strength. Conventional fillers tend to reduce the breakdown strength, however there are indications that well-dispersed nanofillers with appropriately functionalized surface can increase the breakdown strength. Fig. 1 shows results on crosslinked polyethylene with a variety of such fillers. The "TES" treated nanosilica formulation has a breakdown strength at 25°C of 446 kV/mm compared with 269 kV/mm for unfilled XLPE.

Vaughan [2] have shown similar effects with nanoclay fillers in PE, they also demonstrated the effect of particle dispersion on the breakdown strength.

B. Voltage endurance and electrical treeing

For insulators in service, an equally important characteristic is the voltage endurance: the time to failure under a given field. Roy et al [1] have shown this in the same XLPE systems as

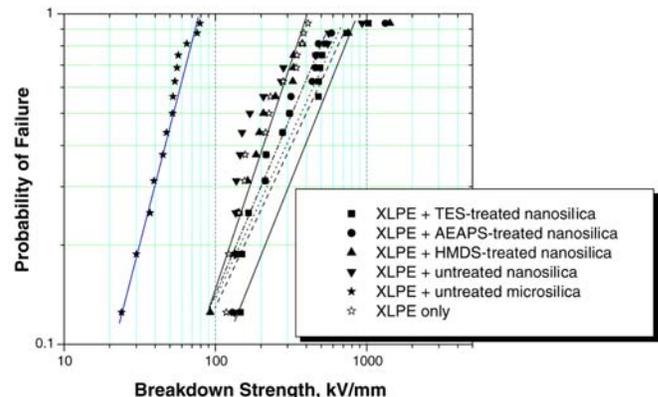


Figure 1. The cumulative probability of breakdown (DC, uniform field) as a function of electrical field for crosslinked polyethylene containing different nanoparticles. TES=Triethoxyvinylsilane, AEAPS – aminopropyl-trimethoxysilane, HMDS = hexamethyldisilazane [1].

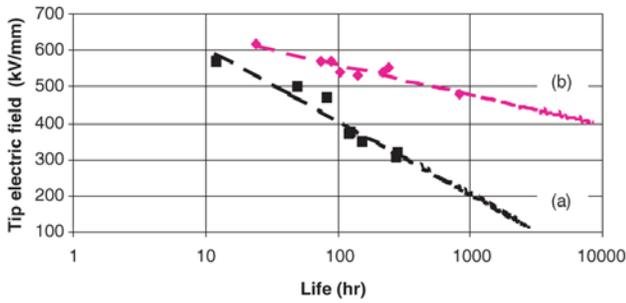


Figure 2. Voltage endurance for 10% loaded epoxy resin loaded with 10% (a) microparticles and (b) nanoparticles of TiO_2 ; after [3].

shown in Fig. 1. Another example of this is shown for filled epoxy resin in Fig. 2. In this work, the insulation was subject to a divergent electric field from a $4\mu\text{m}$ point electrode under a 60 Hz AC field (which may have resulted in electrical trees.) Extrapolation to fields that are used in service ($\sim 10\text{ kV/mm}$) demonstrates the increased lifetime of such systems when using nanofillers.

Imai et al have demonstrated that electrical trees occur in such systems, but are ameliorated by nanoparticles, e.g. Fig. 3. In the nanocomposites, most “bushy” trees, i.e. with a higher fractal dimension, grow in the nanocomposites under similar conditions as the path is continuously interrupted by the presence of nanoparticles. This influence of fractal dimension on time-to-breakdown is well known (e.g. [5]).

C. Water tree growth

Water (or “electrochemical”) tree growth occurs in XLPE cables subject in which the insulation is subject to high humidities. Preliminary results by Hui *et al* [6] suggest that water treeing is also reduced by the introduction of nanoparticles, in this case SiO_2 particles with a trioxovinylsilane coupling agent. This is shown in Fig. 4 (frequency = 1 kHz, 5kV Ashcraft samples, 0.5 m NaCl.) It is less clear how this mechanism operates. The workers suggest that reduction

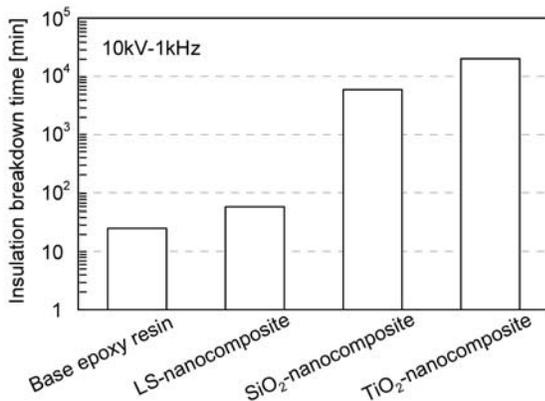


Figure 3. Comparison of voltage endurance under divergent electric field leading to electrical trees (10 kV-1 kHz); (from [4]).

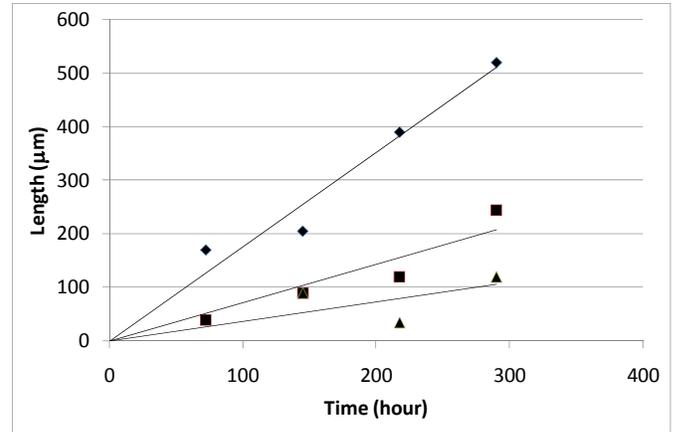


Figure 4. Water tree growth for XLPE- SiO_2 nanocomposite with loadings of: 0% (\blacklozenge), 5% (\blacksquare), and 12.5% (\blacktriangle); (after [6]).

in treeing can be attributed to a scattering effect generated by the interfacial region between the nano particles and polymer matrix; however exactly why such a scattering effect would exist in water trees is not explained.

D. Partial Discharge erosion

Partial discharge (PD) resistance may be evaluated using a rod electrode suspended above the surface of the polymer insulation allowing the measurement of erosion depth. Characteristics of epoxy – titania nanocomposites are shown in Fig. 5.

It was found that both particle and layered silicates have a similar effect in reducing partial discharge erosion. Silane coupling agents are also helpful. As the size of the particle is reduced from $1.6\mu\text{m}$ to 1.2 nm the PD resistance appeared to

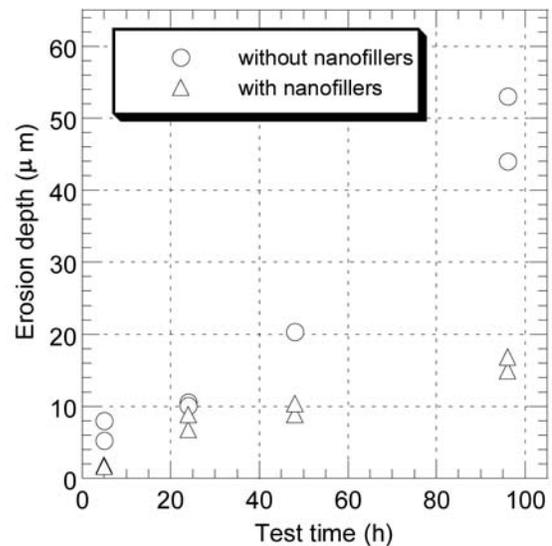


Figure 5. Erosion depth versus PD time for epoxy – titania nanocomposites at 60 Hz, 6 kV (after [4])

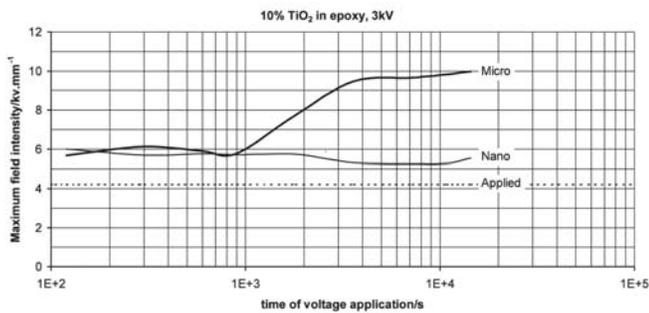


Figure 6. Development of maximum electric field due to space charge accumulation ; (after [8]).

increase. Tanaka *et al* explained this in term of the inorganic materials being more resistive to PD erosion and the dispersed nanoparticles preventing longer higher-energy discharges taking place.

E. Space charge accumulation

The incorporation of nanoparticles also appears to reduce space charge accumulation in some systems. This is somewhat difficult to show as the particles tend to corrupt the measurements (e.g. [7]), but this is largely possible to overcome. Space charge accumulation in an insulator subjected to a high field leads to field variations within the material. Instead of the field remaining constant throughout the material, there are areas where the field can be considerably higher, possibly leading to premature breakdown. Fig. 6 shows how the maximum field increased with time due to the build up of space charge in 10% TiO₂ filled epoxy, a sample approximately 0.71 mm thick was subjected to 3 kV at room temperature leading to an average field of 4.2 kV/mm. After about 15 minutes, the sample filled with microparticles exhibited significant charge accumulation leading to a maximum field of ~ 10 kV/mm. The nanocomposite field remained at ~5 kV/mm. With possible significant developments in HVDC systems, understanding and controlling space charge accumulation is likely to become much more important in such systems. Similar results in the reduction of space charge have been found for polyethylene nanocomposites, e.g. [9].

F. Mechanical tensile characteristics

There is a summary of the mechanical and thermal properties of dielectric polymer nanocomposites in the recently published book on this subject [10].

Most nano-filled composites have mechanical properties that are below those expected from theory; this is largely due to problems of dispersion and ensuring that the mechanical loads are transferred effectively to the nanofillers. Improved functionalisation and processing has improved their properties. Fig. 7 compares the mechanical tensile behaviour of PVA and that filled with carbon nanotubes. Significant improvements in both the ultimate tensile strength and the modulus are observed.

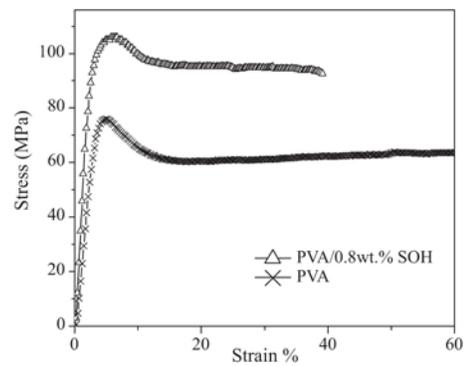


Figure 7. Stress-strain characteristics of PVA with and without 0.8% wt% carbon nanotubes; taken from [11].

G. Thermal expansion

Mismatches between the coefficient of thermal expansion (CTE) of the polymer matrix and the nanofiller can induce micro-cracks that significantly age the material after thermal cycling. Such micro-cracks lead to reduced tensile stresses as the mechanical load is unequally distributed between the host and filler. Rigid nanofillers can reduce the CTE mismatch. Work reported by Huang *et al* among others[12-13] incorporating nanosilica into a polyimide prepared from pyromellitic anhydride and oxydianiline was much lower than that of the near resin. As the filler loading in wt% was increased the CTE decreased in ppm/°C from ~40 at zero loading to ~10 at 30% loading. Irwin *et al* [10] cite similar effects in other systems.

Whilst the examples here cannot hope to represent the full body of work developed since the first reported improvement in electrical properties only 8 years ago [14], the incorporation of nanofillers into insulating systems has given rise to generally positive results. A universal panacea? That is still to be proved. The cost of processing and production may be a hindrance to implementation as may be the natural conservatism of the industry, which has resulted in excellent reliability to date. It seems however, that the optimism and hope expressed in early considerations of the potential of nanodielectrics (e.g. [15]) are being justified by an ever expanding body of experimental evidence.

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VIII. PROGRESS TOWARDS USEFULNESS

In the preceding chapter, more dielectric properties were discussed. Force is to conclude that progress has been made; the facts show this. The facts imply as well that nanostructuration does not come as a solution for every improvement required by the applications.

Circumstances and new events may help in the emergence of applications. Although, nanostructured enamel was studied for a long while already, it is only recently that the technology is commercially offered. Thus, section A below was devoted to these materials.

At last, nanodielectrics, according to their properties, will find their way into electrotechnical applications. CIGRÉ is about to publish a technical brochure [1] in which one complete chapter is devoted to electrotechnical applications. But the scope of applications for nanodielectrics is believed to be much wider. To illustrate this point, section B introduces an example dealing with gas sensing.

[1] T. Tanaka and M.F. Fréchette, Eds. "Polymer nanocomposites – fundamentals and possible applications to power sectors", Technical brochure from CIGRÉ WG D1.24, possibly August 2010.

A. Conventional and nanocomposite enamel behaviour under varying humidity

A characterization study of conventional and nanocomposite enamels with varying the relative humidity (RH%) environmental test conditions has been carried out. Twisted pair specimens have been realized according to the IEC 60851-5 standard procedure [1]. Two kinds of wires have been considered: the first, identified as Conventional Enamel, was insu-

lated using a double layer conventional polyamide-imide non corona resistant enamel having an outer diameter of 1 mm and an enamel thickness of 26 μm , while the second commercial one, identified as Nanocomposite Enamel, was insulated by means of a nanocomposite enamel. This latter is basically composed by a first polyamide-imide enamel layer and a second layer of polyamide-imide enamel containing nano-sized (15 to 20 nm) silica particles: the outer diameter amounts to 1.27 μm and the enamel thickness is 47 μm . All the tested specimens have been conditioned at least 24 h at the same relative humidity level set for the tests. The experimental activity has been carried out applying to the specimens a pure sinusoidal voltage waveform at industrial frequency (50 Hz) having a rms value higher than the partial discharge inception voltage amplitude so to operate in presence of surface partial discharges. Enamel breakdown has been selected as end point criterion and the concerning lifetime values have been collected. Three specimens have been tested for each relative humidity level and voltage amplitude. In Tables I and II the obtained lifetimes relevant to Conventional and Nanocomposite Enamels, computed as the average of the results on the three specimens, are reported.

TABLE I

Conventional Enamel		
V_{test} [V]	RH [%]	Average life time [s]
5300	65	15900
	35	5720
3450	65	40520
	35	105805
2460	65	83760
	35	240840

TABLE II

Nanocomposite Enamel		
V_{test} [V]	RH [%]	Average life time [s]
9000	65	12620
	35	5340
6800	65	32920
	35	33960
5120	65	51940
	35	178500

Because of the extremely long obtained life times at the lowest voltages, the Nanocomposite Enamel has been tested applying voltage waveform having rms amplitudes higher than the ones selected for the Conventional Enamel. Fig. 1 shows the obtained life curves, in a bilog plot, applying to the results the inverse power law. Comparing the obtained results, it is possible to evidence that the Nanocomposite Enamel better behaves than the Conventional ones: at both 65% and 35% of relative humidity the Nanocomposite Enamel shows lifetime values extremely longer than those relevant to the Conventional Enamel: the nano-filler seems to produce a barrier effect

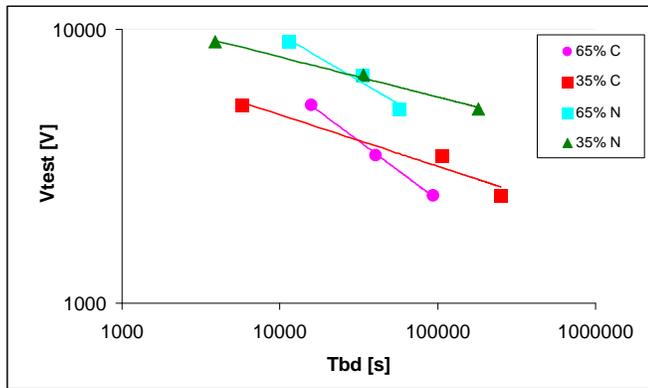


Figure 1. Obtained life curves. C=Conventional Enamel, N=Nanocomposite Enamel

against the PD activity in all the tested conditions as a protective ceramic-like layer. Furthermore, Conventional and Nanocomposite Enamels, at the highest test voltage amplitudes, better behave in wet conditions when the relative humidity is equal to the 65% while if medium/long term performances are considered, the best behaviour is obtained at the lowest relative humidity level. This could be due to the fact that the PD activity and the damaged area dimensions depend on the voltage amplitude and on the relative humidity value:

- the higher the voltage amplitude the higher the PD repetition rate;
- the higher the relative humidity the higher the surface conductivity and the wider the damaged area (Figs. 2 and 3).

If the 35% RH and highest test voltage values are considered, it seems that the effects of the relative humidity on the damaged area dimensions are predominant. In fact at this low value of RH% the PD activity seems to be concentrated in a small area and the times to breakdown decrease. If the test voltage is decreased and the 65% of RH is considered, it

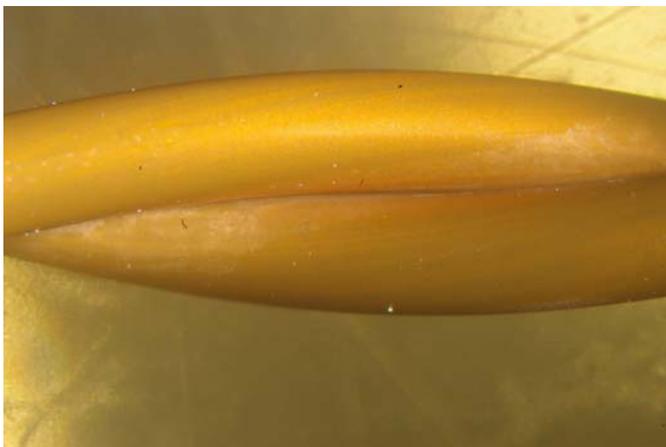


Figure 2. Damaged area: Nanocomposite Enamel, 35% RH, 9000 V.



Figure 3. Damaged area: Nanocomposite Enamel, 65% RH, 9000 V

seems that the relative humidity effect on the surface characteristics becomes predominant. In fact at the 65% of relative humidity, the surface conductivity is higher than at the 35% encouraging the PD activity and partially compensating the PD repetition rate reduction due to the diminution of the test voltage amplitude. This results into a reduction of the times to breakdown.

[1] IEC Publication 60851-5, “Windings wires – Test method – Part 5 Electrical properties”, Edition 3.2, 2004-10.

B. Nanocrystalline metal oxides in gas sensing applications

Recent reports let believe that nanostructured metal oxides are becoming the key materials for developing semiconducting gas sensors with improved gas-sensing properties [1,2]. Despite the availability of several gas detection techniques, metal oxide sensors share a significant part of the \$2.5B market [3]. Simplicity, robustness and low cost are the main advantages of this class of sensors while they suffer from low selectivity, high operation temperature, and low hydrothermal resistance. The exponential progress in nanofabrication techniques makes conceivable the exploitation of their unique properties in gas sensing applications in order to overcome most of the existing materials’ limitations.

Metal oxide gas sensors are semiconductors which convert the chemical interaction of the device surface with a given gas species to a measurable electrical signal through the variation of conductivity. Chemisorption is accompanied by charge exchange between adsorbed gas and oxide surface resulting in a change of surface potential. In an n type sensor, for example, the chemisorbed oxygen creates a potential barrier at the surface of the sensor particles resulting in a depletion layer at grain boundaries. This provides a potential barrier limiting electron movement and conductivity. Any change in oxygen concentration or heterogeneous reaction of oxygen with a reducing gas affects the potential barrier at the grain boundaries and modifies the conductivity [4,5].

A suitable material for a gas sensor must not only have appropriate electronic structure and a good affinity with the tar-

get gases, but must also satisfy a number of other requirements such as manufacturability, hydrothermal stability, and poisoning resistance. Therefore, the choice of material is usually a compromise decision. Simple oxides such as SnO_2 , In_2O_3 , WO_3 [2,5] and mixed oxides such as LaFeO_3 , SrTiO_3 are easily named examples of potential gas sensors [4].

Perovskites with a general formula of ABO_3 , a typical band gap of 3-4 eV, and good thermal stability are an interesting choice for gas sensing materials [1,4]. The size difference between A and B cations makes them flexible to a variety of dopant additions allowing for control of semiconducting properties [4,6].

One of the synthesis and manufacturing challenges of perovskite-based catalysts and sensors is to provide a high specific surface area (SSA) in order to maximize surface reactions and improve their efficiency and response time. Since SSA increases sharply with decreasing crystallite size, nanostructured materials are of great interest. In addition, when the crystallite size is small enough to be comparable to the thickness of the charge depletion layer, the sensor conductance becomes very sensitive to the target gas because only a few thermal activated carriers will be available [7].

High energy ball milling (HEBM) is an efficient technique for preparation of a wide range of ultrafine ceramic powders. By optimizing the process parameters, a powder with a desired composition and a very low crystallite size (down to 10 nm) is achievable. In addition, the resulting powder is comprised of hard agglomerates having a very high density of grain boundaries. The technique is easily scaled up and offers a reasonably low production cost compared to the other preparation routes.

Considering the requirements for gas sensors and the capabilities of the HEBM technique, this technique has a great potential to develop highly sensitive and low cost nanoperovskite sensors. In addition to significant practical advantages such as mass production, low cost and waste-free, a number of other advantages could be conceivable:

- It has been shown that the edges and corners are the active sites for gas/solid surface reactions [8,9]. The HEB-milled materials are subject to heavy plastic deformations during synthesis leading to a higher quantity of edges and corners which could improve the receptor function of the sensors.

- Oxygen diffusion coefficient is an important factor that controls the equilibration time between bulk point defects and surrounding gas. This coefficient being significantly higher in grain boundaries [1,10] indicates that the response time must be significantly shorter in HEB-milled sensors.

- Despite the HEB-milled powders being comprised of nanocrystallites, the agglomerates usually have a wide size distribution varying from 40nm to a few microns. This will improve the permeability of thick coatings and facilitate the washcoating process; a commonly used process in the catalysis industry.

Many questions remain to be answered in this domain.

Some major ones are formulated below:

Grain boundary effect: A HEB-milled oxide is basically comprised of large agglomerated (micron size) with crystallites size down to 10 nm and a great amount of grain boundaries. Oxygen diffusion coefficient is significantly higher in grain boundaries:

How the grain boundary diffusion can affect the conductivity of the agglomerates?

Coating: Coating is an issue in manufacturing of low cost sensors. In order to develop a marketable sensor, a coating capable of meeting the thermal shock, adhesion, and vibration testing requirements is needed. Washcoating is considered a potential method due to its simplicity and adaptability to industrial processes.

How can we improve the adhesion of coating and reduce the gap of thermal expansion coefficient between the coated layer and substrate (alumina is usually used as substrate) without compromising the sensitivity of the sensor?

Thermal stability and Poisoning: Although we expect to reduce the operation temperature of sensors by increasing the surface area and modifying their morphology, some sensors must work at high temperatures. In general, nanomaterials with lower recrystallization temperature do not have very good thermal stability. This issue could be addressed by adding grain growth inhibitors during milling. The addition of grain growth inhibitors may affect the electrical continuity of the sensing layer. So:

How the thermal stability of a nanocrystalline mixed oxide can be improved?

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IX. CLOSING REMARKS

The preceding festive writing stemming from a Halloween gathering amazes ... It stands as a testimony of various aspects of the situation and/or domain.

On the verge of the years 2000, there was for sure a change of paradigm and many scientists adapted and engage in this new research. Force is to say that the dielectric community, at least involving electrotechnical applications, had lacked enthusiasm and vision towards the end of the nineties. The emergence of a new class of dielectrics, ca. 2001 and first experimental data evidencing nanocomposites as dielectrics in 2002 [1] stirred things up for the last decade.

This document shows as well that a multidisciplinary approach is a must with this topic, and it has worked here. Science starts to make progress when a vision is elaborated; formulating the right questions and/or asking various scientists to share their views on some unknowns is a first major step to leap into the future. Nanodielectrics have definitively a future. This is supported by the present document.

It is John Fothergill who came up with this idea of panacea. In those times, there would be a roving person going from one city to the other offering syrups, ointments, powders, and some miraculous bottles that were presented like universal remedies, efficient to heal all, ... that is a panacea.

Therefore, adapted to our field, the question arose “Are nanodielectrics a panacea?”. *The answer to that question is no!* In some cases, an electrotechnical application does not require the use of nanodielectrics. In some other cases, the meagre gain exhibited by the use of nanodielectrics does not warrant its use. What is true however is that sometimes the use of nanodielectrics may offer a substantial and dominant gain in a non-dielectric property, e.g. weight.

It is not a panacea, but progress as made explicit and the still opened questions surely support a real potentiality that lies ahead, a potentiality that started to transform itself into applications.

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ACKNOWLEDGMENT

The authors acknowledge the sponsorship of their respective company or institution. A special thanks to Dr. A. Besner, Head – Sciences des matériaux for allowing this activity and Dr. D. Faubert, Director of the Institute, for talking briefly at the “Brainstorm at the institute”. Let us underline that year 2010 is the 40th anniversary of Hydro-Québec’s research institute (IREQ).

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