Progress, Understanding and Challenges in the Field of Nanodielectrics

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Keywords: nanodielectrics, nanomaterials, polymer nanocomposites, inorganic/polymer nanocomposites, insulating materials, dielectrics

The field of nanotechnology has emerged as one of the most active technological areas worldwide, and interest in nanodielectrics has grown rapidly as a potential new generation of HV insulating materials with unique properties. Experimental progress in this field and the challenges facing practical implementation needed to be commented. A wide range of materials (largely nanofillers in a polymer matrix or intercalated or exfoliated layered natural or synthetic inorganics within a polymer matrix) are being evaluated by universities and industry, and several significant improvements in important electrical, mechanical, physical, and thermal properties confirmed. This suggests that a number of HV insulation applications could benefit from such materials. However, some limitations have been identified which need to be understood and corrected or accommodated, e.g. the role of the nano-inorganic-polymer interface.

When the concept of nanodielectrics was introduced in 2001, it emerged in the middle of several developing activities associated with nanotechnology. After some 5 years, it turns out that the nanotechnological effort has been increased and widened. This is easily illustrated by considering the blooming of the number of conferences and meetings dealing with nanotechnological aspects.

Although no outstanding and revolutionary commercial success has been confirmed over this period, investments have continued to flow into nanotechnology research and development, which is somewhat surprising. It is maybe because science is at a turning point. For a long while, science has forced to explore in the limits of the largest and the smallest, with a will to push beyond. But it is no more the ultimate. Along the years has emerged the realization that lateral levels (at some dimensions) of interest lied along the paths, some science was there to be discovered, and it corresponded to a wealth of numerous social-economic benefiting applications.

For nanostructured materials, some breakthroughs were produced, in particular in reference to nanocomposites and multifunctional thin-films. It is suspected that many developments and findings are kept confidential, but some major steps were realized over the period, specially in seeking properties that do not obey the laws associated with the bulk behaviour.

The story is only beginning so why then the present type of exercise? Indeed, the rise of interest if not its shift was so quick, it produced a non-negligible amount of data in a very short period of time. From there, risks are emerging too and there is still much magic surrounding the field. At least two elements were stressed in regard of these points. Measurements and properties were found to depend greatly on the material synthesis particularities and reproducibility and phenomenology are very much sensitive to recipes and quality of the end-products. If there is magic it is very much varying with content and morphology, and there is a serious need for quality control of the developed materials.

Figure 1 offered an interesting insight in the field. Though not based on a extremely precise analysis, it illustrated clearly two developing streamlines. Nanofiller must be added to microcomposites if one wants to obtain solid dielectrics with electrotechnical superior performance as compared to conventionally-filled polymeric matrix. This does not discard research activities dealing exclusively with nanofillers. Those are necessary for more fundamental understanding and yet they may be an alternative pushing for the adoption of thermoplastics in replacement of thermostets in an environmental context.

Some discussion made explicit our lack of sufficient understanding about the situation. The conclusion is that we ignore more than we know, and this state-of-situation usually prevents a clear and direct access to applications. Though it is always hoped from a new discovery or concept, that it will bring uniqueness, thus new solutions leading to extraordinary gains as opposed to incremental ones, some discussion pointed out at some dual or two-fold phenomenologies that make think that there is underground or hidden potential to be realized.

Nonetheless, HV electrotechnical applications were envisaged. An instant snapshot based on the emerging data was put forward. It is essential nowadays to question right away how the outcome of research could fit in and benefit the applications. Even now, the conclusion is that these new findings could find its way to very practical problems, add-ons, etc. However, it is much too early to estimate profitability. But, some needs for developments were formulated.

Finally, the limited survey indicates that there is a strong need for quality control of the "nanodielectrics" and accrued documented knowledge linking the nanostructural morphology and the macroscopic observables.
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The field of nanotechnology has emerged as one of the most active technological areas worldwide, and interest in nanodielectrics has grown rapidly as a potential new generation of HV insulating materials with unique properties. Experimental progress in this field and the challenges facing practical implementation will be commented. A wide range of materials (largely nanofillers in a polymer matrix or intercalated or exfoliated layered natural or synthetic inorganics within a polymer matrix) are being evaluated by universities and industry, and several significant improvements in important electrical, mechanical, physical, and thermal properties were confirmed. This suggests that a number of HV insulation applications could benefit from such materials. However, some limitations have been identified which need to be understood and corrected or accommodated. The role of the nano-inorganic-polymer interface (dielectric and electronic properties, space charge mitigation, band-gap and charge injection effects, and morphology effects) will be considered. Based on this analysis, the ultimate potential that might be realized via nanodielectrics will be envisaged.

Keywords: nanodielectrics, nanomaterials, polymer nanocomposites, inorganic/polymer nanocomposites, insulating materials, dielectrics

1. A Brief Perspective

When the concept of nanodielectrics was introduced in 2001(1), it emerged in the middle of many developing activities associated with nanotechnology. After some 5 years, it turns out that the nanotechnological effort has been increased and widened. This is easily illustrated by considering the blooming of the number of conferences and meetings dealing with nanotechnological aspects(2). It is noteworthy that some past existing items have been adapted to a new flavour. It is also necessary to recall, as pointed out twice earlier(1)(3), that some past observations and phenomenologies had to do with a nanometric scale but then there was no focus as today with nanotechnology. Again, there are a spectrum of effects that goes with intervening at the nanometric scale. Sometimes, it brings a small positive increment on a property; in others, it elicits new phenomenologies.

Although no outstanding and revolutionary commercial success has been confirmed over this period, investments have continued to flow into nanotechnology research and development, which is somewhat surprising. It is maybe because science is at a turning point. For a long while, science has forced to explore in the limits of the largest and the smallest, with a will to push beyond. But it is no more the ultimate. Along the years has emerged the realization that lateral levels (at some dimensions) of interest lied along the bulk behaviour. Seeking properties that do not obey the laws associated with the bulk behaviour.

Efforts have continued to elicit great progress relatively to superplasticity and ductility of superstrong nanomaterials. The mechanical properties of nanocrystalline materials often exhibit super strength, superhardness and enhanced tribological characteristics, but at the moment(5), focus is on obtaining in addition a substantial ductility and superplasticity. That would be a unique combination.

Developments have accrued relative to magnetic effects. Efforts were devoted now to incorporate supermagnetic and ferromagnetic behaviours to polymer nanocomposites(6).

Many strategies are unfolding to resolve the limit imposed by the brittleness of nanocrystalline ceramics. For this, reinforced second phases are used to develop nanometric-scale composite materials. Due to the extraordinary properties of carbon nanotubes, these are considered as incorporation to ceramics (to metals and polymers too). However, the potential of this action has not yet been successfully demonstrated(7). Besides, much effort will have to be deployed to obtain and ascertain high purity single wall carbon nanotubes(8). Much interest stays with the unfolding and application potential in microsystem technology(11). For the field of nanodielectrics and their applications, the area of polymer nanocomposites remains the driving stemming inspiration and the provider of the materials and their molecularly tailored materials. For nanostructured materials, some breakthroughs were produced, in particular in reference to nanocomposites and multifunctional thin-films(9). It is suspected that many developments and findings are kept confidential, but some major steps were realized over the period, specially in seeking properties that do not obey the laws associated with the bulk behaviour.

For the field of nanodielectrics and their applications, the area of polymer nanocomposites remains the driving stemming inspiration and the provider of the materials and their
characterization. To this effect, we note the continued effort invested in the organization of the Polymer Nanocomposites Symposium(12) and the emergence of the first symposium on characterized nanocomposites(13). Some other applications of importance considered are: gas barrier, oxygen barrier, fuel tanks, films, environment functionalizing. Some other applications of importance considered are driving the market while there is a lot of material protection and flammability reduction.

A considerable amount of data on nanodielectrics suddenly appeared in the recent years marking some progress. While there appears to be some very promising results to-date, there are also many results, though interesting, which are disappointing. The application of nanodielectrics to electronics and photonics is well established, but not so to HV insulation such as used in generators, motors, transformers, cables, capacitors, bushing, HV supplies, or as insulation in a multitude of aerospace and military applications. In fact, however, fillers (of fumed or colloidal or other specialized origin), on the nanometric scale, have been used for as long as 30 years, in limited applications, though nonetheless, very successfully. As with many antioxidants, voltage stabilizers, stress-grading additives, or similar molecular-scale additives, generally the use of “nanodielectrics” has been highly proprietary, since their use has been instrumental in superior insulation performance or processing or overall cost advantage or some other desirable property.

For the moment, nanodielectrics deal mainly with a matrix containing added nanostructures. In that sense, it recalls very strongly earlier work and achievements relative to reinforcements and fillers. Properties of polymers were found to be significantly improved by adding solid particles to the thermoplastic resins. It is a well established field and some recipes are well known. The work of Cherney may certainly be offered as a reference(22). Some features of the situation must be recognized. A diversity of properties can be affected, and sometimes more than one at a time are changed. The dimension of the added reinforcement and filler ranges in the micrometric size to submicrons. Also, it is usual that the filler may reach 10 to 40 % of the compound weight. Is the knowledge acquired for this micrometric situation be transposed when the nanometric scale is involved? It is very tempting, yet it is not so, at least to a large extent.

Such a high-content of the filler, many times an inorganic, may bring about extra cost and extra weight. The question here is “Can these issues be addressed by replacing high content by high specific area associated with the nanoparticles?” It turns out that nanoparticles with high aspect ratios have proven to be good reinforcing agents in polymeric materials. Among all nanoparticle reinforced composites, the most widely investigated systems are based on silicates and clay particles(23). When dealing with the nanoparticles, many additional and dominant parameters come into play. Filler size, shape, and the homogeneity of the particle distribution become critical parameters, with an accrued importance on filler/matrix interface coupling nature and quality. The nature of the interface will be affected to a great extent by the chemical synthesis route

<table>
<thead>
<tr>
<th>MATRIX</th>
<th>NANO-FILLER</th>
<th>PROPERTIES / FIELD / APPLICATION</th>
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<tbody>
<tr>
<td>PVAI</td>
<td>Carbon nanotube</td>
<td>Thermomechanical and electrical properties, Functionalized; taken from Ref. (14)</td>
</tr>
<tr>
<td>Polyvinyl</td>
<td></td>
<td></td>
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<tr>
<td>alcohol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>Cellulose whiskers</td>
<td>Mechanical performance Functionalized; taken from Ref. (14)</td>
</tr>
<tr>
<td>Thermoplastic</td>
<td>Modified</td>
<td>Low mass, cost effective, improved surface quality Automotive molded body parts</td>
</tr>
<tr>
<td>Olefin</td>
<td></td>
<td>Commercialized on car; taken from Ref. (15)</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Carbon nanotube (CNT)</td>
<td>All things being equal, smaller fillers achieve the required stiffness at lower filler concentrations</td>
</tr>
<tr>
<td></td>
<td>Nanoclay (NC)</td>
<td>Less weight % CNT than NC; taken from Ref. (16)</td>
</tr>
<tr>
<td>PET</td>
<td>Intercalated clay</td>
<td>Polycondensation Functionalized; taken from Ref. (14)</td>
</tr>
<tr>
<td>Polyamide, e.g. PA-6</td>
<td>Exfoliated silicates</td>
<td>70 % higher tensile modulus 130 % higher flexural modulus 50 % lower oxygen permeation Commercially important for automotive, aerospace, food packaging; from Ref. (14)</td>
</tr>
<tr>
<td>Rubber</td>
<td>Carbon black</td>
<td>Strength, elasticity and abrasion Structural engineering: taken from Ref. (17)</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Silicate layers (Synthetic, 1-nm thick with high aspect ratio of 200)</td>
<td>Matrices for carbon or aromatic fibers reinforces composites used in aerospace industry High modulus and high temperature performance Taken from Ref. (18)</td>
</tr>
<tr>
<td>Epoxy</td>
<td>TiO\text{2}</td>
<td>Best improvements on stiffness, impact strength and wear resistance at a content of 4 vol %. Taken from Ref. (19)</td>
</tr>
<tr>
<td>Nylon-6</td>
<td>SiO\text{2}</td>
<td>Rigidity and toughness improved at an optimal content of 4.3 wt %. Taken from Ref. (20)</td>
</tr>
<tr>
<td></td>
<td>Pre-treated</td>
<td>Higher dynamic viscosities Superior storage moduli at HF</td>
</tr>
</tbody>
</table>
employed to produce the nanocomposite and how the nanoparticles were fabricated, pre-treated\(^{(39)}\), and compatibilized.

The driving knowledge relevant to the situation involving nanometric-scale particles is closer to what was acquired from developing and dealing with special additives\(^{(26),(27)}\) for electrotechnical and non-electrotechnical applications and from compounding polymer blends\(^{(26),(27)}\). Table 2 offers a comparison between a typical case involving nanoclays and conventional filler. Much of the information was taken from the literature\(^{(14),(28)}\).

Profitability of going “nano” cannot be generalized. Yes, there are some trend principles, e.g. high aspect ratios bring about significant property enhancement, smallness of the filler ensures less surface distortion, lower amount of filler minimizes density. For the rest, each business case must show merit. For instance, in the automotive industry, reduction of weight is very important\(^{(15)}\).

This annotated appreciation will be developed along several streamlines pinpointing at some drawbacks and weaknesses of the newly emerging dielectric materials. Impact on the electrical insulation arena will be also discussed with identification of some required developments and needing achievements.

### 2. What Do We Know about Nanodielectrics?

Generally, nanodielectrics might encompass all solid materials where one dielectric material is incorporated inside another and has one dimension in the nanometric range (from 1 to 100 nm). It might include spherical, ellipsoidal-shaped particles, rod-shaped particles (e.g. nanotubes), monolayers, thin layers, or larger layered particles (such as natural or synthetic clays) where the layers have been penetrated by a second dielectric phase (intercalation) or even fully separated (exfoliation). Largely, however, much of the work to date on nanodielectrics has focused on spherical particles (typically oxides) made by, for example, a fuming process, or intercalated or exfoliated natural or synthetic clays (e.g. montmorillonite). Very closely related, however, are some block copolymers and some polymer blends, where one of the blocks or polymers is of nanometric size and the resulting qualities are highly synergistic. For example, polyurethanes made with nano-sized rigid polymer blocks, can achieve remarkable mechanical properties, and where used in demanding electrical applications, excellent superior insulating qualities.

Table 2. Comparing characteristics of composites with different-scale fillers

<table>
<thead>
<tr>
<th>CONVENTIONAL FILLER</th>
<th>NANOCLAY FILLER</th>
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<tbody>
<tr>
<td>Size : 1 μm</td>
<td>Size : 1 nm</td>
</tr>
<tr>
<td>Cste* volume # : 1 particle</td>
<td>Cste volume # : 10^2 particles</td>
</tr>
<tr>
<td>Surface or coupling agents</td>
<td>Chemical modification of layers</td>
</tr>
<tr>
<td>Aspect ratio &lt; 10</td>
<td>Aspect ratio 50 - 500</td>
</tr>
<tr>
<td>Loading &gt; 20 %</td>
<td>Loading 2 - 10 %</td>
</tr>
<tr>
<td>Dimensions : 1x100x100 μm</td>
<td>Size : 1x100x100 nm</td>
</tr>
<tr>
<td>Surface area : 0.7 m^2/g</td>
<td>Surface area 600 - 700 m^2/g</td>
</tr>
<tr>
<td>Source : Mineral, synthetic</td>
<td>Source : Natural, synthetic</td>
</tr>
<tr>
<td>Structure: Crystalline, amorphous</td>
<td>Structure : layered</td>
</tr>
<tr>
<td>Ex : TiO_2, Al_2O_3, SiO_2, ZnO</td>
<td>Ex : Montmorillonite most usual</td>
</tr>
<tr>
<td>Availability : yes</td>
<td>Availability : yes</td>
</tr>
<tr>
<td>Cost lower</td>
<td>Cost higher</td>
</tr>
<tr>
<td>Drawback: less performing</td>
<td>Dispersion sensitive</td>
</tr>
</tbody>
</table>

Table 2 offers a comparison between a typical case involving nanoclays and conventional filler. Much of the information was taken from the literature\(^{(14),(28)}\).

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or 2 other properties are sometimes examined along the study of dielectric properties, e.g. glass transition temperature, Young modulus, degree of crystallinity, impact strength, thermal conductivity, thermal expansion, etc. However, there is a diversity of dielectric aspects which were examined, and often, a single study would address many of these aspects: observations on electrical treeing, dielectric spectroscopy (permittivity and losses), photoluminescence measurements, surface tracking and erosion, space charge measurements, breakdown, conduction and polarization/depolarization processes, volume resistivity, etc.

Of those, surface degradation and electrical treeing in presence of corona were maybe the first and most important concerns to be dealt with. Earlier study of Henk (39) and following work (40)-(43) have revealed a substantial positive effect (easily from 2 times to more than 7) from filling a polymer matrix with nanofiller. Based on known phenomenologies linked with the presence of micrometric-size filler in insulating matrices, some peculiar observations were noticed when these measurements were carried out using nanometer-size filler. Using dielectric spectroscopy, one can conclude that different matrix materials with the same nano-fillers behave differently in their permittivity and losses (44).

In epoxy nanocomposites, both the interface polarization and dipolar relaxation contributions can be clearly seen and polarization is also enhanced by increasing the loading of fillers. In polyethylene nanocomposites, interfacial polarization also can be observed, but spectrally it does not change its position and intensity with increasing temperature. It was found also that the losses at very low frequency is highly dependent on the initial functionalization of nanoparticles (33). Imai et al. (45) observed that the permittivity and tan δ decreased when base epoxy was transformed to nanocomposite epoxy. Dielectric properties of epoxy nanocomposites containing TiO₂ and ZnO fillers were studied by Fothergill et al. (46), and they found that the dielectric spectroscopy results showed very little dependence upon the particle material, only the size appeared to be important. These results were considered to support that the dielectric properties of such nano-filled composites were controlled by Stern-Gouy-Chapman layers around the particles.

The behaviour of some polymer nanocomposites in relation to space charge were investigated. Overall, from these studies, e.g. (47)-(48), there seems to be a trend emerging. Space charge inception field decreases as compared to that of the base material. When a nanocomposite is involved, space charge was found to increase at low field and to decrease at high field (47). It was observed that some space charge behaviour was directly linked and was responding to chemical impurities associated with the compatibilization of the nanosilicates, and varied sensibly with the purification procedures (49). In the authors’ view, results from dielectric spectroscopy would be correspondingly affected. Pre-treatment of the nanoparticles is too a strong parameter in determining the outcome performance (50)(51).

But the ultimate test, some sort of technological appraisal, is the performance of the nanocomposites comparative to that exhibited by a microcomposite, that is a polymer matrix containing a micrometer-size filler. Figure 1 presents the emerging trend relative to breakdown strength and surface corona resistance. It is meant to be illustrative as it includes several different study parameters. Here the comparison is intended to be with a conventional-filled matrix, e.g. epoxy with 55-65 % wt. of silica. Nelson et al. have shown that for a similar, yet low weight % (5 %), the breakdown strength of the nanocomposite exceeded greatly that of the microcomposite (52). Here a series of studies was consulted to establish a phenomenological trend for the electrical breakdown (52)-(54) and for the corona resistance (45)(53)-(58). In this exercise, some data were weighted somewhat intuitively.

In both cases, the use of low-content nanofiller may give an approximative equal performance as compared to conventionally-filled matrices. But the real advantage comes with the use of both nano and micro fillers at the same time. This advantage can be felt much more in the property of corona resistance of surfaces, where more than doubling the resistance is observed in a system of epoxy + quartz + nanoclay (33). Although the understanding of the chemical route in preparing these nanocomposites and imaging of the nanostructures indicate that the nanoclay reinforced the resin where the microsize filler was not present, and in these regions, special bonding is privileged due to a large surface ratio, other speculative details provide complimentary explanations and paths for further reflections (59).

Some concepts were advanced and formulated to explain some of the phenomenology surrounding the polymer nanocomposites and their performance. The interfaces (60)(61) and interaction zones (55)(62)(63) are certainly keys to understanding, yet the effects of the chemical route for synthesis and changes in morphology are too lightly neglected. To put a little bit of nano in the matrix still sounds like adding some magic powder with a waive of the hand. The real question is “Are we adding more defects than the material can handle?”

In the flurry of activity over the past five years, a wide spectrum of materials and details of preparation have been studied and a wide spectrum of behaviour has been reported, ranging from significant improvements in dielectric (and other) properties, to modest improvements or even worse. Given the variations examined to-date, it is not unsurprising that our understanding of their causes and of the behaviours observed, is rather limited. To advance the cause of nanodielectrics, it will be important to separate and understand the individual roles of the nanoparticle and surrounding polymer matrix, and the interactions and synergistic effects between them.
To-date, the particles evaluated have typically been oxides (such as TiO$_2$, Al$_2$O$_3$, ZnO, SiO$_2$) or intercalated or exfoliated synthetic or natural clays or other layered inorganics. The specific role of these different inorganic particles which have widely different permittivities and shapes (i.e. widely different local electric stress enhancements), will be of great interest in terms of performance at low and high electric fields where potential electron scattering, charge injection, quantum tunnelling, or even simple inhibition of progressive endurance failure modes such as electrical treeing, are considered as taking place. Some of these nano-particulates have exhibited substantial improvements in properties such as breakdown, even in their pristine (untreated) condition; but benefit further when coupling agents or compatibilizers are used; thus first and second order effects need clarification. As noted above, some nano-fillers are very effective at loadings of 1-2 % but benefit decreases as loading is increased whereas other nano-fillers become effective at higher loadings, with flat performance as loading increases. Others show superior (synergistic) performance with both nano and micro-sized particles present together. Insight into why there are such differences and whether particle chemistry plays a role will be enlightening.

Our understanding of the structure and properties of the interface region are similarly, if not more, limited. This is the region from the surface of the nanoparticle outwards, involving the matrix polymer and its contents, affected by the presence of and bonding to the nanoparticle, up to where these effects have significantly disappeared. Electrical and dielectric properties (e.g. a Gouy-Chapman-type extended double layer) are believed affected, while physical (crystallinity, glass temperature) and mechanical properties appear to be relatively unaffected or even significantly affected. Indications are that the level and type of bonding of the matrix to the nano-filler (as controlled by a coupling agent) plays a significant role in the physical and mechanical properties, since it controls the conformational structure and organization of the polymer chains and consequently properties like crystallinity. This will also affect transport and relaxation behaviour and therefore electrical and dielectric properties; but, especially for relatively non-polar polymers, these will also be affected by presence of ionic and non-ionic polar constituents drawn to the polar/higher field nano-particle interface. Unreacted coupling agent, compatibilizer, antioxidants, processing additives, or other impurities may respond to this attraction. For these reasons, though we do not yet know specifically which or how, with nanodielectrics it is found that permittivity may be significantly lowered, space charge behaviour significantly reduced, relaxation times very low, and generally unique electrical properties. Resolving the role of the interface region will undoubtedly be of importance in setting nanodielectrics on a secure technological and fundamental footing.

Lastly, the practical implementation of nanodielectrics will be helped by improved understanding of the behaviour up to and at high electric fields: space charge behaviour, electron scattering, and endurance behaviour, to name a few.

### 3. On the Fancies and Unknowns

Considering the feeble amount of hard evidence found in the dielectric literature, and with the further realization of the impact of controlled characteristics of the microstructure on the unfolding macroscopic properties, force is to conclude that the state of real understanding does not match the level of speculative saying and proposals put forward. This is not mentioned in a negative sense, but rather in a way to stress the need to pursue the lacking information to verify the on-going work hypothesis. Thus, it is consequent to observe that the state of situation conveys and entertains magic, fancies, misconceptions, misunderstanding stemming strongly from unknowns. It is the aim of this section to feed slightly the discussion.

For instance, it is a fancy to envisage to fill a polymer with several % wt. of nanometer-size particles. It is meant more than a few. Before reaching a percolation limit or a maximum content of surfaces fitted in a solid (specific surface area inversely proportional to specific gravity times particle diameter, see for instance$^{(19)}$), there are other considerations that come much quicker. The first of it, and the most important, is really how many defects or non-optimized regions can be incorporated and tolerated in a bulk? The image of a single particle (seldom very well rounded and with undefined surface electronic states) well localized in space and surrounded by an homogeneous interphase is a conceptual chimera. Much effort and advancements in the field of polymeric matrix containing nanoclays provide confirming information$^{(21,60)}$.

The review produced by Okamoto$^{(64)}$ contains a wealth of information regarding several properties and how they are affected by the addition of nano-fillers. Some general trends can be observed. Very often, the property is found to increase between 0 and 10 % wt. After that amount, the curve featuring the property is often seen to saturate, sometimes there is a down shift. Often too, the rise up to 10 % is quasi linear, usually, between 0 and 2 %, the rise is steep. When several properties are studied, the variation of each single property is not necessarily the same, for instance one may not be affected and stays constant. This is observed even when the properties are in the same category, e.g. strain, stress yield, Young modulus. Finally, in some cases, the property seems to be enhanced even past the 10 % wt. There would seem essential to clarify this situation since the use of a mix of both micrometric and nanometric fillers appears to be above competition for dielectric performance. Superior performance was also observed for other properties than dielectric$^{(19)}$. But, there seems to be several polymer-layered silicate nanocomposites that exhibit an enhanced performance as compared to their microcomposites counterparts, in areas other than dielectric$^{(60)}$.

There can be many factors affecting the relation between % wt. and the outcome, but the experts usually consider that for nanoclay, complete exfoliation can only occurs for % wt. of less or equal to about 1 % (see Ref. (21) for instance). There are some considerations relative to the packing volume fraction yet at some point it is the platelets that are not able to rotate freely, and limits the content. Above 1-2 %, exfoliation will start to be limited, surface ratio will decrease, and risk that nanostructure will transform and/or elicit morphological defects will increase.

Relative to nanocomposites using nanoclays, one recognizes 3 types: intercalated, flocculated, and exfoliated. There can be a mix of different types. Without going into many details, the basic difference between intercalation and exfoliation is the presence of tactoids (stacks of platelets), resulting in a structure showing platelets very closely disposed (between 1-2 and 8-9 nm) with a binding realized by the intercalant. There would seem, based on experimental evidence obtained at IREQ, that the presence of tactoids in an epoxy bulk containing a large weight content of
quartz (crystalline SiO$_2$ up to 60 % wt.) would in fact lessen the corona resistance of a surface as compared to that obtained when the nanoclays are fully exfoliated. Figs. 2 (b) and (c) show TEM micrographs of the samples put to test. In the SEM micrograph (Fig. 2(a)), blobs of polymer illustrate non-optimized regions. Is it a different phase? At least several layers of polymer or compatibilizer macromolecules aggregate. Fig. 2(c) makes explicit the fact that we are (most probably) dealing with tactoids.

Specialists are still questioning the differences and evidences of stating the different types (66), and furthermore, there is always the overall distribution to be quantified. This sample was submitted to experimental conditions as described earlier (55), and the results showed a decreased performance in face of surface resistance to partial discharges. Intercalation and exfoliation makes indeed a great difference in some macroscopic properties. At first glance, a reduction in surface ratio could be considered as an affecting parameter. But the performance remained superior to that corresponding to a microcomposite and nanoclays which are polyionic, thus hydrophilic, are still found not to interact with the micrometric quartz but to reinforce the epoxy zones.

Purification and pre-treatment of the nanoparticles affect the surface functionalization and will also drive via the surface ratio the type and number of molecular interactions with the matrix. For instance (35), clay platelets, with 40 % atoms on the surface, have high surface energy and are hydrophilic. The molecular adsorption at their surface causes the formation of two layers. A first layer is on the order of 6 nm thick and it is a solidified inner layer. There is also a second layer, from 6 to ca. 100 nm, an outer layer with increasing molecular mobility. Tanaka et al. also introduced a multilayer model (62). Also, there are many evidences that purification, pre-treatment and functionalization of nanostructures (35,49)-(52x63) (and references therein). But as it was put forward by Fréchette (35) in 2004, the resulting mesoscopic interphase zones will extend these bonding layers and interfacial thicknesses and will be determined by other factors including crystallization, preferential nucleation and formation of different crystal phases, 2D versus 3D effects, shape and alignment effects, multiplied and distributed energy traps. This thought is schematized in Fig. 3.

The present model puts emphasis on the interphase and the different zones of influence. It is a multiparametric situation since the nanostructure (nature, size and form will dictate its inter-relation), the nature of the matrix, the methodology employed, the chemical routes, the percent-content of the additive (one particularity is the fact that the effect occurs for low %-content), the nature and importance of the interphase (being defined as the transitional zone between 2 distinct zones (e.g. nanoparticle to polymer), the effect of the collectiveness and linearity in face of the integrated macroscopic observables, all influence the outcome. It is speculated here that the bulk material is in some instances nanostructured with effective blocks consisting of influence zones. This would be the analogy if the interphase is dominant. The treatment of the situation will be analogous to the case of the nanomaterial consisting of a great number of grains (influence zones) and the grain boundaries (zone mismatches). The latter could be considered as a conceptual interface.

There is much hard evidence linking morphology (say at the mesoscopic scale in some range: free volume, micro-spherulite, orientation and presence of chains) with macroscopic properties. It is a false secret that even in the synthesis process, nucleation is affected by the presence of the nanostructures. For instance, Maiti et al. (67)(68) have studied the crystallization behaviour and morphology of neat PP-MA (maleic anhydride grafted polypropylene) and three different nanocomposites (PPCNs) in detail. They found that clay particles act as a nucleating agent for the crystallization of the matrix PA-MA, but that the linear growth rate and overall crystallization rate is not influenced significantly by the presence of clay. Exfoliated nanostructures are found to favour heterophases and the formation of different crystalline forms. For instance, this was found to be the case for Nylon 6 with
organically modified montmorillonite. Very low levels of clay resulted in dramatic increases in crystallization kinetics relative to extruded pure polyamide and the nature of the surfactant used, could drastically affect the nanocomposite morphology and properties. Finally, there is sufficient evidence, e.g. (35), (71)-(73), to conclude that breakdown and space charge, two macroscopically observable dielectric properties, are influenced by the nanoscopic to mesoscopic morphology.

It is usually contended that the addition of nanoclay to a polymer matrix ends up reducing the free volume. The understanding on that is that the total free volume depends (at least and at first) on the total clay surface capable to absorb the macromolecules. So far only one report on free volume measurement in relation to a dielectric study was produced. It indicated that for a system of epoxy containing nano TiO$_2$, on the contrary, the free volume was found to increase. Was it the way that the nanoparticles were purified and chemically pre-treated that ended up in a functionalization not optimizing the surface ratio reactivity to the polymer macromolecules? The point would have to be resolved eventually since free volume is recognized to play an important role into the initiation of discharging. Let us mention that the compatibilizer is usually found to affect greatly the free volume.

4. Electrotechnical Applications and Potentials

It has long been recognized that HV insulation can have a major leverage in HV equipment design, through higher operating stresses, higher operating temperatures or higher thermal conductivity, and superior mechanical properties, for example, or through improved electro-thermal-mechanical endurance qualities, or through higher efficiency (lower losses). These qualities translate into smaller, more reliable, more efficient equipment and, of course, the all-important, lower cost, both for the initial equipment and for long term operation. Over the past two decades, improvements in some of these areas have been realized but often they have been incremental. The advent of nanodielectrics appears to afford an opportunity for some major improvements of insulation materials and systems, though clearly not all nanodielectrics have been optimized to the point where all are likely to succeed.

4.1 New Solutions and Generic Possibilities

This section wants to initiate an exploration of the intrinsic potential of nanodielectrics. Although it is not clear up-to-now that some uniqueness will stem and provoke a solution to an unsolvable problem, force is to admit, from a glance of the nanostructured material field, that highly interesting avenues shine.

Free volume in solid dielectrics is an hindrance, e.g. (75). Much research indicates that the incorporation of nanoclay at 2 % wt. in polymeric matrices reduces the free volume, so that would be a benefit. However, there were recently some data showing the opposite, an increase of the free volume for a matrix of epoxy containing nano TiO$_2$. Still controlling the free volume is a most interesting possibility, especially in reducing the dimensions of the microvoids.

Of other possibilities, it is noteworthy to mention the adaptability of the Lotus effect to dielectric surface. Though there are proposals of material coatings which repel strongly water, the Lotus effect features structural surface morphology (nanostructures on microstructures) that prevents water or liquids to interact with the surface. Other opportunities are: controlling and field grading at surfaces, control of asperities and roughness at surfaces, controlling a volume parameter, e.g. grading the dielectric constant, tailoring very high or low permittivity dielectrics.

Not only dielectric properties are of interest, there are insulation system applications such those at low temperature using superconductivity that would benefit greatly from enhanced and adapted mechanical and thermal properties of the insulating solid materials, e.g. epoxy. Mechanical defect and counter-performance of the material at low temperatures are making the demonstration an unsuccessful venture. Another line of improvement could come from the fact that several properties at the same time may be modified, it would be an advantage since a commercial dielectric must comply with a matrix of requirements.

Finally, in this brief appreciation, let us introduce the possibilities of new two-fold phenomenologies. This type of manifestation would consist of a new behaviour brought upon by the nanostructure with the additional impact of improving a macroscopic property. There are several examples of this including in other fields like gas barriers with their zigzag diffusion path. One dielectric speculation is made explicit below.

Follows the report of some experimental observations that deal with a situation where the surface discharge is affected by the bulk composition. The epoxy composition was found to affect the discharge phenomenology at the surface surrounding a triple junction.

The electrode arrangement is depicted in Fig. 4. A bulk of epoxy is sandwiched in a plane/point/plane electrode configuration. The side contact of the point electrode with the surface of the bulk constitutes a triple junction. AC voltage was applied. Light emission at the junction and its surrounding was monitored using an ICCD camera. Light can be localized with respect to the electrode and software allows some analyses. The scheme of measurement gives access to discharge having a power as low as 0.005 µWatt.

An epoxy bulk has been prepared made of a mix of resin, a 60-% weight load of SiO$_2$ and a small percent additive consisting of nanoclay (see (55) for the synthesis). The bulk was set to form a

Fig. 4. Photograph and scheme of the gap arrangement and electrodes configuration
gap arrangement as shown in Fig. 4 and ac stress was applied when air pressure was at 500 kPa. Under these conditions, the triple junction became active. However, a distinctive behaviour drew our attention when the discharge behaviour was compared with that involving an epoxy without nanoclay. When the epoxy with nanoclay is used, the discharge surrounding the triple junction exhibits instability as a function of time. In the Fig. 5, ICCD recordings of the light activity when discharging occurs are introduced. Each frame lasts 100 ms. Figures 5(a) to (d) exemplify the instability characteristics: The discharge elongates, fractionates in several fragments. These instabilities were not present in the discharge phenomenology observed with an epoxy without nanoclay. The reference bulk of epoxy had the same surface finish.

Considering that it is likely that the permittivity of the nanoclay will somewhat differ, and that it is recognized that the nanofiller will temper with the details of the surface finish, it is speculated that both items will join to intervene into the management of the surface charge, maybe producing a dielectric discretization at the surface. So the dual phenomenologies would be discharge fluctuation at the surface due to discretization, a fluctuation that would help in reducing the degradation impact and augment the surface corona performance. It is understood here that the nanoclay has reinforced the epoxy regions where no micrometric inorganic was found and this resulted into an accrued surface corona resistance (55).

4.2 Electrotechnical Opportunities and Possible Impacts

This section wants to initiate an exploration of the intrinsic potential of nanodielectrics. Although it is not clear up-to-now that some uniqueness will stem and provoke a solution to an unsolvable problem, force is to admit, from a glance of the nanostructured material field, that highly interesting avenues shine.

Five general electrotechnical opportunities can be identified from the R&D work on nanodielectrics reported through 2005. These have involved the use of spherical inorganic nanoparticles dispersed in different polymer matrices or the use of intercalated or exfoliated natural and synthetic clays and layered inorganics, also dispersed or intercalated by different polymer matrices.

1. Insulation for HV rotating equipment

Excellent partial discharge (PD), in short-time tests, has been achieved using fillers and intercalated/exfoliated inorganics in epoxies for conventional insulation. Although rigorous physical models do not exist to explain the apparent improvement in pd resistance, these inorganic materials, such as Al2O3, are better able to bind with the host resin matrix and do not suffer from the poor wettability of mica platelets. Further, several “high temperature” thermoplastics (e.g. polyetherimides) that might offer unique fabrication methods for rotating machinery groundwall or turn insulation or for advanced vpi (vacuum pressure impregnation) resins, as well as opportunities for higher machine temperature operation have been proposed or used in limited applications. The corona resistance qualities have been achieved at lower loadings of such inorganics and can result in superior (very desirable) mechanical performance to conventional larger sized corona resistance fillers. While these innovations are focused on producing more compact insulation designs resulting in machines with higher energy density, attention must also be paid to the consequences of increased electrical stress in the endwindings of the machine. Lack of focus on this feature in some of the earlier machines employing so-called corona resistant materials resulted in significant pd problems in the end arms. However, the use of nanodielectrics should also enable the solution to such potential problems since these materials offer new possibilities in designing stress grading compounds that have superior electrical and thermal performance to existing silicon.

Fig. 5. ICCD recordings showing light intensity and patterns closely by the triple junction; Epoxy with nanoclay, all taken at 8.97 kV ac; Conditions : (a) frame 21, (b) frame 22, (c) frame 24, and (d) frame 400
carbide-based formulations.

The same considerations extend to wire insulation either enamels, powder-coated, or extruded where corona resistance must be complemented by good mechanical, physical and thermal qualities, and often, conventional (micron) fillers compromise the end product.

(2) Insulation for HV extruded cables Excellent short and long term breakdown has been achieved with spherical fumed fillers in a high performance XLPE, exceeding the performance of same unfilled XLPE\(^{(5)}\). This has been achieved at 5 % loadings; and with a particular coupling agent, give improved high temperature performance compared to XLPE. Electrical space charge behaviour in such nano-particle-filled XLPE indicates electrical properties that may give them unique qualities for dc cable operation.

While enhanced electrical and thermal properties resulting from the inclusion of low fill ratios of nanodielectrics offer promise for more compact cable designs and high temperature operation, the prospects for improved accessory design are also critical. With the exception of mechanical damage to cables, terminations, joints and splices represent the highest risk to reliable operation of underground transmission networks. This situation arises because of the high electrical stress design of most accessories and the critical dependence of workmanship in their successful installation. The use of nano-filled materials with enhanced breakdown and electrical field grading capabilities will be beneficial in designing more robust and reliable accessories. Another advantage may lie in the lower permittivity which would lower cable capacitance.

The use of finely-dispersed clays and fillers such as (fumed) SiO\(_2\), chemically bonded to the XLPE matrix via specific coupling agents such as the vinyl silanes, has been known and reported in the literature since soon after the invention of XLPE for HV cables using chemical crosslinking in 1963\(^{(81)}\). Soon afterwards, the use of fillers for optimized XLPE dc cable design was examined experimentally and theoretically by EPR\(^{(82)}\). In the intervening years, significant effort has taken place to upgrade the unfilled XLPE, paralleled by the introduction and improvement of co-extruded semicon's, purification of the resin, innovative filtration of the melt, on-line diagnostic techniques (e.g. ir and x-ray), and for higher voltages, vertical extrusion. New, nano-filler-based XLPE will need to be tested in experimental cables (at lower voltages) and subjected to rigorous short and long-term electrical and mechanical tests, as discussed in IEEE-ICC and CIGRE over the past decade. In particular, it must be compared against premium tree-retardant and water-tree-retardant XLPE cables used by the leading extruded HV cable manufacturers worldwide.

(3) Insulation for capacitors Intercalated inorganics at 2 % loadings in polypropylene, the dominant leader of polymer films used in power and industrial capacitors, has shown improved dc breakdown performance over unfilled polypropylene. Given that conventional, extruded PP film can operate at ac electrical stresses of 635 V/m and higher, achieving higher operating stresses has always been a challenge and nanodielectrics, of this or other inorganics, may offer the potential of reaching higher long term operating stresses.

Polypropylene film, used in modern all-PP HV capacitors, is made by blown bubble or draw and tentering methods, and is characterized by critical biaxial orientation involving 2D lamellar crystallization during the cooling stage after extrusion of the isotactic PP resin melt. Specific rheological properties of the PP resin are required in order to achieve the PP film qualities to give the high breakdown strength for such application and the (natural, morphologically controlled) texturing of the film surface in order to facilitate liquid impregnation. How readily nano-filled PP resin can match/exceed these qualities, or whether the nano-filler might replace or enhance the role of the nucleating agents which are used, are questions to be addressed. Another pervasive issue with PP-based capacitors, are the very low losses required in ac power capacitors, one of the primary applications. Somewhat different qualities are needed for PP film used in metallized capacitors, which must also be assessed.

(4) Insulation for low and medium voltage extruded cables Non-crosslinked, polycrystalline, thermoplastic polyethylene has also shown improvements in breakdown strength via the use of nanodielectrics, using both spherical inorganic particles and intercalated inorganic layered fillers, and may offer enhanced performance for PE used in low and medium ac voltage applications; and, based on space charge measurements, certainly for dc applications.

The fillers can be tailored to give exceptional water resistance and thus enhance capability for direct burial usage. Presently, ethylene propylene rubber (EPR) insulated cables are favoured in applications where more severe mechanical stresses are anticipated, e.g. in installations with tighter bending radii. However, EPR cables have higher losses, thus, the use of nanodielectrics as an additive to more flexible XLPE insulation may permit a new class of XLPE cables with improved mechanical properties.

(5) Insulation for molded HV components and accessories Different improvements derived from the use of nano-fillers in thermoplastics, thermosets, and rubbers, have been identified, which, though more modest, indicate that they could supplant present materials, because of one or more advantage they hold. Though not identified specifically in the R&D work to-date, many of the advantages/improvements identified above could reasonably be applied to accessories such as cable splices and terminations.

(6) Potential impacts Already there is evidence that nanodielectrics are able to significantly enhance mechanical performance and somewhat enhance thermal performance, without sacrificing electrical properties, as typically happens with micro-fillers. Indeed, ac electrical performance is significantly enhanced in a few cases; while space charge studies on several nanodielectric systems reveal them to have potentially unique properties of importance to dc application. The impact on other important properties such as physical, dielectric, environmental, and effect on processing and overall cost, have not been significantly addressed to date. Thus, the evidence to-date suggests that nanodielectrics might first become important for HV insulation because of their superior balance of properties. As their construction begins to be optimized, their enhanced properties may likely improve further. The potential impact in these five electrotechnical application areas are as follows:

Rotating Equipment
Design improvements
Smaller size
Improved reliability
Lower overall costs
from the academic community; and, disappointingly, involvement activity has been rising rapidly. Much of this interest has been taking place over a relatively short period of time and interest and other hand, improvements in understanding and testing have been thermal stability, have received minimal attention to-date. On the key properties, such as endurance and long term chemical and followed. However, clearly, some properties have faltered and other nanodielectrics, leading to optimism that HV applications will demonstrated experimentally by the formulation and use of nanodielectrics will be integrated into new designs or will permit design having globally an extra performance.

**Table 3. Link between the nanodielectric aspect and its potential impact on applications**

<table>
<thead>
<tr>
<th>Nanodielectric Quality (vs existing)</th>
<th>Potential Application Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unique</td>
<td></td>
</tr>
<tr>
<td>Significant lowering of space charge</td>
<td>dc designs</td>
</tr>
<tr>
<td>Enhanced</td>
<td></td>
</tr>
<tr>
<td>ac breakdown and endurance</td>
<td>reduced insulation</td>
</tr>
<tr>
<td></td>
<td>reduced overall size</td>
</tr>
<tr>
<td></td>
<td>improved design</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>improved design options</td>
</tr>
<tr>
<td>Permittivity</td>
<td>lower capacitance</td>
</tr>
<tr>
<td>Slightly enhanced</td>
<td></td>
</tr>
<tr>
<td>Thermal rating</td>
<td>improved design margin</td>
</tr>
<tr>
<td>Processing (mixing/extrusion/etc.)</td>
<td>improved performance and reliability</td>
</tr>
<tr>
<td>Uncertain</td>
<td></td>
</tr>
<tr>
<td>Environmental</td>
<td>plus or minus</td>
</tr>
<tr>
<td>Conclusion</td>
<td>potential impact in several areas</td>
</tr>
</tbody>
</table>

HV Extruded Cables

- 254 V/m operation
- Superior dc cables

Insulation for Capacitors

- 1270 V/m ac designs
- Improved processing
- Higher temperature capable PP film

Insulation for Low and medium Voltage PE Cables

- Superior water and environmental performance
- Insulation for Molded Applications, including Accessories
- Options for enhanced all-round performance
- Improved reliability

Table 3 is offered as a summary of the author’s vision linking what is brought upon by “nanodielectric” quality with an informed guessed impact on oriented applications. It is expected that profitability stems from application associated with unique or very enhanced property exhibited by some nanodielectrics. It is an oversimplification, and a bit too early an estimate, since some nanodielectrics will be integrated into new designs or will permit design having globally an extra performance.

**5. Needs for Development**

The improvement of several important properties has been demonstrated experimentally by the formulation and use of nanodielectrics, leading to optimism that HV applications will follow. However, clearly, some properties have faltered and other key properties, such as endurance and long term chemical and thermal stability, have received minimal attention to-date. On the other hand, improvements in understanding and testing have been taking place over a relatively short period of time and interest and activity has been rising rapidly. Much of this interest has been from the academic community; and, disappointingly, involvement by industry, unlike the field of electronics and photonics, has been relatively limited.

Against this background and with cognizance of the limited understanding for nanodielectrics noted above, we suggest that focus needs to continue in two areas:

- The fundamentals of nanodielectrics, establishing the separate and interactive roles of the nano-filler, the polymer matrix, and the interface region, and the generality of behaviour exhibited by those nano-fillers investigated to-date plus other model or different nano-fillers.
- The validation and optimization of nanodielectrics for specific applications.

Some of the key areas of attention are considered to be:

- Establishing the individual and interactive roles of nano-filler particle, polymer matrix, and interface region using Design of Experiments (DoEs).
- Correlation with interface models such as Gouy-Chapman and polymer physics models.
- Documentation of pretreatments, purification, coupling agents, comaptibilizers, preparation methods, and material assays.
- Enhanced characterization methods.
- Extension of testing to the range of properties required for anticipated applications, including performance/endurance testing.
- Optimization of nanodielectric insulation application candidates, to provide a picture of their potential “process window”.
- Extension/scale-ups of sample preparation and testing to match anticipated applications (e.g. fabrication of corona-resistant nanodielectrics structures simulating different applications; preparation of thin, biaxially-oriented nano-filled IPP for potential capacitor application; extrusion of model nano-filled XLPE cables).

In conclusion, of course, we suggest that the dielectrics/insulation community should continue to keep an eye on the progress, methodologies and best practices of the “nanotechnology” community.

**6. Closing Remarks**

This brief overview has allowed to appreciate the state of emergence of this new field tagged as now “Nanodielectrics”. Force is to conclude that, as in the past, it is a different market, namely the automotive and packaging ones, that is driving the material development which will serve our field.

The story is only beginning so why then the present type of exercise? Indeed, the rise of interest if not its shift was so quick, it produced a non-negligible amount of data in a very short period of time. From there, risks are emerging too and there is still much magic surrounding the field. At least two elements were stressed in regard of these points. Measurements and properties were found to depend greatly on the material synthesis particularities and reproducibility and phenomenology are very much sensitive to recipes and quality of the end-products. If there is magic it is very much varying with content and morphology, and there is a serious need for quality control of the developed materials.

Furthermore, the same batch material should be used in several studies in order to provide a matrix-property assessment of the
performance. Indeed, application wise, a new material must satisfy an ensemble of varied requirements.

Figure 1 offered an interesting insight in the field. Though not based on an extremely precise analysis, it illustrated clearly two developing streamlines. Nanofiller must be added to based on an extremely precise analysis, it illustrated clearly two

an ensemble of varied requirements.

performance. Indeed, application wise, a new material must satisfy

necessary for more fundamental understanding and yet they may be an alternative pushing for the adoption of thermoplastics in replacement of thermosets in an environmental context.

Some discussion made explicit our lack of sufficient understanding about the situation. The conclusion is that we ignore more than we know, and this state-of-situation usually prevents a clear and direct access to applications. Though it is always hoped from a new discovery or concept, that it will bring uniqueness, thus new solutions leading to extraordinary gains as opposed to incremental ones, some discussion pointed out at some dual or two-fold phenomenologies that make think that there is underground or hidden potential to be realized.

Nonetheless, HV electrotechnical applications were envisaged. An instant snapshot based on the emerging data was put forward. It is essential nowadays to question right away how the outcome of research could fit in and benefit the applications. Even now, the conclusion is that these new findings could find its way to very practical problems, add-ons, etc. However, it is much too early to estimate profitability. But, some needs for developments were formulated.

Finally, the limited survey indicates that there is a strong need for quality control of the “nanodielectrics” and accrued documented knowledge linking the nanostructural morphology and the macroscopic observables.

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(2) http://www.nanotech-now.com/; in particular, see the “events” section.


(10) See POSS technology at http://www.hybridplastics.com/


(12) International symposia on polymer nanocomposites science and technology, first (2001), second (2003), and third (2005), held in Boucherville, QC, Canada.

(13) First international symposium on nanostructured and functional polymer-based materials and nanocomposites, Desden Germany (2005)


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“Workshop on cryogenic dielectrics”, presented in conjunction with CEIDP 2005, Nashville, USA (2005)


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