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Nanodielectrics

A “Universal” Panacea for Solving All Electrical Insulation Problems ?

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Abstract — This text summarizes the keynote presentation that is based on the full-length paper of the same title. Dr. Fréchet’s oral presentation should not be seen as a summary of the “Brainstorm paper” but a glance at some major accomplishments, hindrances and still remaining questions relative to nanodielectrics. Are nanodielectrics a “universal” panacea*? The answer to that question is no – but they’ve got a lot of potential!

Keywords- *polymers, nanocomposites; nanodielectrics; dielectrics*

The presentation will unfold along the three topics identified here.

* The first reference that JCF could find for the expression “Universal Panacea” comes from “The Haunted Quack - A Tale of a Canal Boat” by Nathaniel Hawthorne, written in 1831. Quackery is a derogatory term used to describe the use of unproven or fraudulent medical practices in which a universal panacea may be sold as the cure to all ills.

I. THE CONCEPT OF NANODIELECTRICS

The concept of nanodielectrics is reviewed. What are they? What is so special about this concept? What should we expect with these materials?

A nanodielectric is defined as a multi-component dielectric possessing nanostructures, the presence of which brings changes in one or several of its dielectric properties. In addition to nanometric structures, active mechanisms and processes at the nanoscale must be present that are responsible for these changes. Considerations will be given as to how the many mixing aspects interplay and contribute to the emergence of the resulting behavior. The interfacial regions are felt to be particularly important and although there may be situations in which the building blocks are more important than the interface, workers have given much weight to the concept of the “interaction zone.” Thus, the interface and its role will be emphasized; the role of physics and chemistry at the interface may determine the behavior of the composite. The electrical

structure of the interface has been represented by John Lewis as a Gouy-Chapman diffuse double layer and by Toshikatsu Tanaka and colleagues as a 4-layer structure surrounded by the host polymer which retains its “normal” properties. Whilst these models may apply in some cases, their verification has not been universally confirmed. In many cases, some of the dramatic improvements in properties may be explained by a simple non-polar, low conductivity bonding of nanoparticles to the surrounding polymer matrix. This will be discussed.

Also of interest is the case of ceramics where novelty in the dielectric properties is more obviously observed in view of the well determined grains and their boundaries. The reactive grain boundaries that dominate 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); and v) tendency to adsorb impurities and their precipitation at the reactive sites. Examples of such properties will be given.

II. NANOSTRUCTURATION AND MACROSCOPIC BEHAVIOR

Links between nanostructuration and resulting material macroscopic behavior will be discussed.

The “holy grail” in this quest is to seek the understanding of how the characteristics of the nanofiller relate to the endpoint “nanoeffect”, observed as a modification of one or several macroscopic dielectric properties.

The nanoparticles possess intrinsic properties, which are subsequently varied and/or modified by the fabrication process, purification stages and post surface treatments. Handling and storage conditions may also be important, for example, humidity has been found to react strongly with epoxy nanostructures.

This topic will be discussed by considering the case of polymer nanocomposites containing nanoclay (PNCs). Whilst the structure of the nanoclay complicates the mixing and the interpretation of the resulting behavior, such nanodielectrics constitute a major industrial-based source of applications. Nanoclays are basically layered silicates with variants in composition and types of impurities. The layers form stacks, which must be prepared for dispersion into a polymer matrix. The nanoclay is therefore usually “intercalated”, which results in the enlargement of the distance between planes.

For enhanced dielectric performance, it was shown that the initial presence of the intercalant must be reasonably removed and/or replaced by the matrix polymer. Dielectric response may be used to characterize this process as it is very sensitive to local charges at the stack location. It is very difficult to exfoliate nanoclays. This point will be explained as well as those linked to the limitations on nanoclay concentrations (approx. 1%). Mixing the nanoclay into a polymer most of the time requires the use of a compatibilizer, which may also affect the dielectric properties.

For dielectric applications the polymers of choice are hydrophobic PE or PP, which are thermodynamically immiscible with hydrophilic clays. The way out of this predicament is a two-step clay modification involving intercalation and compatibilization. Intercalation not only changes the clay character (from hydrophilic to hydrophobic), but also expands the interlayer spacing (i.e., between clay platelets in a stack) from about 1.2 to 3 nm. Compatibilization is performed by the incorporation of polar-group terminated macromolecules added to the polymer and pre-intercalated clay during melt compounding. In simple terms, some polymeric substance (sometimes in a substantial amount) has been added to the polymer matrix, and this can modify the endpoint dielectric properties. Compounding the material samples will further intercalate/exfoliate the nanoclay, and will involve the establishment of nano-, micro-, or macrometric morphologies, which in turn will affect or specify the dielectric behavior. Even cutting the samples in certain ways may affect the dielectric performance.

During the last few decades, with the growing pressure for material recycling, there has been a continuous switch from thermosets to thermoplastics. Industrially, only layered materials, mostly natural or synthetic clays with platelets ~0.7 to 2.5 nm thick, are of interest for PNCs. Owing to the nanometer-size, the clay-containing PNCs show markedly improved mechanical, thermal, optical and physico-chemical properties (heat resistance, barrier properties, flammability, etc.) when compared with neat polymers or composites.

Specific results involving a matrix of polypropylene (PP) containing organoclay will be detailed. Incorporation of a small amount of organoclay has large effects on the mechanical and barrier properties, but only moderate effects on the dielectric behavior. The electrical and dielectric test results show the importance of the ionic layer surrounding the nanoparticles. By contrast, it seems that the intrinsic properties of the clay platelets (e.g., chemical composition or aspect ratio) have a smaller effect on the dielectric behavior of PNCs.

III. CURRENT STATUS

Where are we now with nanodielectrics?

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 researchers 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”.

The major research effort to date has been dominated by the influence of polymer nanocomposites. In this framework, interfaces are dominant. Partial nanostructuration of polymer nanocomposites was found to improve partial discharge resistance, to suppress space charge formation and affect charge relaxation, and to prolong the treeing lifetime. In many cases, it is not understood how many properties may be altered beneficially simultaneously. This is particularly important for

industrial applications were a material must satisfy a matrix of properties. Many of these properties are not dielectric; they may include chemical, mechanical and thermal properties for example. Thus, there is the possibility to tailor dielectric properties but only to improve the overall performance in some instances.

Some dielectric properties will be reviewed here, and they consist of some examples related to electrical breakdown strength, voltage endurance and electrical treeing, water tree growth, partial discharge erosion, space charge accumulation, mechanical tensile strength, and thermal expansion.

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 are being justified by an ever expanding body of experimental evidence.

It would seem that the low-achieved degree of self-assembly for now precludes the observation of more novelties. In this direction, progress in the design and use of dendrimers will be instrumental in the near future.

For the next steps of development, it will be important to consider nanofillers that exhibit extraordinary properties. This approach may provoke real emergence of novelty and/or marked deviations from extrapolated property improvements. Carbon nanotubes with or without encapsulation, silica flakes or graphene planes, insulating nanotubes like boron nitride, to mention a few, fall into this category.

IV. CURRENT STATUS

The future lies ahead. The wealth of information on so many aspects presented in various sections of this paper, demonstrate the important future for the field involving the nanostructuring of dielectrics.