Paper #369: Overview of Polymer Nanocomposites as Dielectrics and Electrical Insulation Materials for Large High Voltage Rotating Machines

Z. Han [*], Randy Garrett
Siemens Power Generation, 5101 Westinghouse Blvd, Charlotte, NC 28273, USA
* han.james@siemens.com

ABSTRACT

Polymer nanocomposites are defined as polymers in which small amounts of nanometer size filers are homogeneously dispersed and will have a potential significant impact on materials mechanical, electrical and thermal properties etc. In power industry, electrical insulating polymers usually incorporate inorganic fillers to achieve specific electrical, mechanical, thermal properties and reduce cost. Therefore in recent years, the polymer based nanocomposites with excellent electrical and thermal properties have drawn more and more attention to the research and industry people in the field of dielectrics and electrical insulations, especially for large high voltage rotating machines such as Rotors and Generators. There is always a demand for materials engineers in this area to develop better electrical insulation systems that can operate at higher temperatures and grater electrical stress or to develop systems that can be made for significantly lower cost and higher efficiency.

The progress, advantages, limitations, and current problems of using polymer nanocomposites as dielectric materials in high voltage generator applications will be discussed in this review. Several research groups worldwide have now been able to document some significant improvements that potentially can be made especially in the electrical and thermal properties of polymer nanocomposites through the incorporation of nano-particulates. However, there is still a long way to go in terms of understanding the mechanisms of the enhancement effect in nano dielectric materials and its successful commercial applications in the power generation industry.

I. INTRODUCTION

This topic might have been defined as nanometer size dielectrics to investigate dielectric phenomena in nanometer scale. However, it didn't become clear that there may, indeed, be advantages to be gained in the field of electrical insulation area until further works from Henk in 1999[2], and Frechette in 2001 [3]. From Frechette's work in 2001, the nanodielectrics were used to explore nanometrics dielectrics and dielectrics associated with nano-technology and to produce molecularly tailored materials. This concept seems to be associated with nanostructured ceramic fillers and tailored nanocomposites. The potential application of nanocomposites dielectric materials in the area of manufacturing high voltage rotating machines didn't draw too much attention from the researchers and engineers in this business and research area until the pioneer experimental work by a US/European team [4,5]. Prof J. Keith Nelson from RPI and Prof John C. Fothergill from High Voltage Dielectrics Lab at the University of Leicester had done a series of experimental work to obtain a fundamental understanding of the way in which nanoparticles interacted in a polymer (epoxy resin) matrix to change the dielectric properties. The understanding of the mechanisms controlling the properties of these uniquely structured materials is the key to taking advantage of nanocomposties as advanced dielectrics especially the "interfaces" between the inorganic fillers and the organic based polymers such as epoxy resin systems. Interfacial control is critical: achieving good coupling between the inorganic filler and the base polymer is necessary for success. Therefore, the present thrust is both to try to optimize the benefits and, perhaps more importantly, to provide a better understanding of the physics and chemistry of the interface on which these materials rely. This is important since it is the basis on which nanodielectrics can be designed in an informed way.

Since then, the contribution is concentrated on the use of nanoparticles (defined loosely as material having one dimension less than about 100 nm) incorporated in a polymer matrix. So, within this class of hybrids, there is a great deal of opportunity to tailor the properties of the resulting material to specific applications.

There is the promise of new and enhanced properties being derived from the interactions of nanofillers with polymer matrices; the complexity of nano-, meso- and micro-materials interactions provide a large number of variables with which to tailor properties, which would be interesting to both scientists and engineers.

The interfacial region between nanoparticles and the epoxy matrix is a high volume fraction because of the high surface-to-volume ratio of nano inorganic fillers. In comparison with conventional micrometer-sized fillers, the same volume fraction of nanofillers contains million-fold number of nanoparticles. Therefore as a result, much of the base polymer in nanocomposites is located at interfaces. It is well known that the interface in a composite has a significant role in influencing the properties of electrical insulation materials.

In the power industry, electrical insulating polymers incorporate inorganic fillers to achieve specific electrical, mechanical, thermal properties and to reduce the cost. There is a constant demand for materials engineers to develop better electrical insulation systems that can operate at higher temperatures and greater electrical stress and that can be made for significantly lower cost and higher efficiency. Table 1 provides an overview of some of the viewpoint of insulating systems currently under investigation.

Table 1 Examples of nanocomosite system under development

Base Polymers	**Nanomaterials**
Polyolephins	Clays, inorganic nitrides and inorganic oxides
Epoxy / Phenolics	Inorganic oxides, carbon nanotubes
Elastomers	Carbon nanotubes
Ehylene-vinyl copolymers	Graphite
Polyethylene terephthalate	Ceramics
Polyamides	
Polyimides	
Polystyrene	
Polyvinyl alcohol	

From the viewpoint of insulating systems most of the activity has been on clays and inorganic nitrides and oxides (particularly AlN, BN, SiO_2, Al_2O_3, ZnO and TiO_2 etc.). In particular, epoxy nanocomposites - epoxies in which small amounts of nanometer size fillers are homogeneously dispersed - have shown potentially improved electrical and thermal properties in comparison to more conventional composites and have commanded more attention in the field of dielectrics and electrical insulations, especially in manufacturing large high voltage rotating machines such as turbine generators [6].

Historically the epoxy resin based composites had been widely used in both the power industry and the microelecronics industry because of their generally superior electrical, mechanical and thermal properties along with their economical and convenient processability. In power industry, for most generator manufacturing business, epoxy is the most popularly used materials for stator groundwall insulation system. The properties of these epoxy/inorganic filler composites depend on the nature of the inorganic filler such as its chemical and physical composition, size, shape and dispersion in the epoxy matrix etc [7]. Among these properties enhancements, perhaps the most important property of nanocomposites is the change in electric strength which is found when the filler particles attain nanometric dimensions. However, it was not until recently, we started seeing the publications and research activities on the electrical properties improvement of epoxy/nanofiller nanocomposites used for high voltage generator stator groundwall insulation. Although the interest here is primarily the electrical properties of this new class of material, it is likely that many of the applications will also take advantage of attendant changes in other attributes, particularly thermal conductivity[6,8]. This paper will be focusing the topics of dielectric properties and thermal properties of the newly formed epoxy/nanofiller nanodielectrics used for the large high voltage rotating machines such as generators. There is only a small number of industry oriented research centers worldwide is now working on this area [4,5,6,8]

II. Dielectric Properties of Nanodielectrics

As discussed previously, perhaps the most important property of nanocomposites is the change in electric strength which is found when the filler particles attain nanometric dimensions. This contrasts with the situation for conventional micro-particles where substantial reductions in electric strength are typical as a result of the weak interfaces and defects which are involved. This has been demonstratged by the recent work from Prof. Nelson [9]. This is illustrated in Fig 1 where the DC quasi-uniform field electric strength of a biphenol epoxy resin system is depicted with both micro- and nano-particulates of TiO_2 used to form the composites. The impact of the size of the filler, at the same nominal loading of 10% by weight, is clearly evident when the micro- and nano-composites are compared.

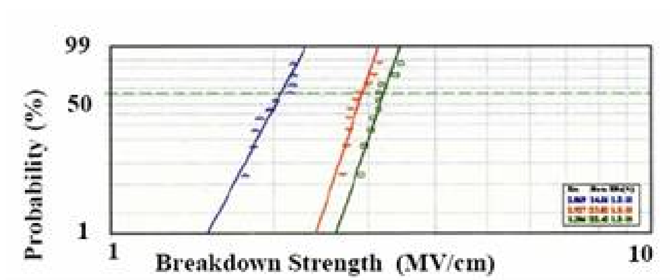

Fig.1. Breakdown probability plots for nanocomposites using recessed specimens on Epoxy- TiO_2 composites.

Analogous results for the voltage endurance under non-uniform field conditions are depicted in Fig 2 where the improvements are dramatic. These endurance curves are plotted in terms of the maximum field at the tip of the point/plane gap and show over 2 orders of magnitude improvement in the voltage endurance in the epoxy systems.

NSTI-Nanotech 2009, www.nsti.org, ISBN 978-1-4398-1783-4 Vol. 2, 2009

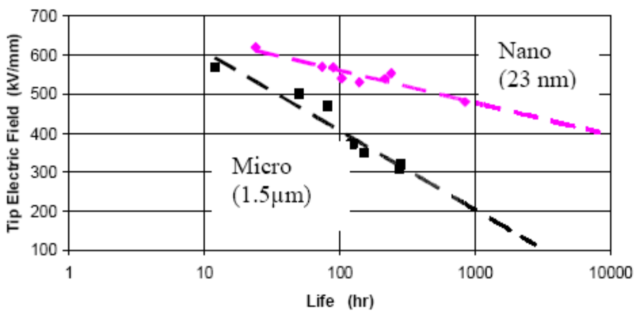

Fig.2. Voltage Endurance characteristics for nanocomposites using 4 µm tip/plane electrodes on Epoxy/ TiO_2.

The researchers from Prof Gary Stevens group (Gnosys UK) in the UK had also done some pioneering experimental work on this area. In Prof G. Stevens work [8], both nano BN and nano Alumina had been used in the incorporation of epoxy resin systems in order to enhance the electrical properties of Epoxy/filler composites. Boron Nitride (BN) has been widely used to enhance the dielectric properties of the groundwall insulation system used for generator. BN has a reasonably high electrical resistivity (1015 ohm cm) and breakdown strength (53kv/mm), which suggests a good insulating material. Moreover, it has a small relative permittivity, about 4.0 which is close to that of epoxy resins and much smaller than the other ceramics. These outstanding properties suggest BN is suitable to be used in epoxy composites as a filler to potentially improve the electrical properties. Conventional alumina is another commonly used filler to improve electrical, mechanical and thermal properties in insulating composites, however, there is little in the published literature about the application of nanometric size alumina in electrical insulating composites. In his research, these two interesting fillers were incorporated within the same epoxy resin to examine their electrical behavior.

It is found from his research that it is always difficult to obtain a fine dispersion of small particle fillers in polymer matrices because they aggregate easily and are difficult to separate due to strong surface interactions. In this research, both conventional stirring and ultrasonic processing were used to obtain uniform dispersion of the inorganic fillers in the matrix. Electric properties including dc current and dielectric constant have been measured in the frequency domain from 10^{-2} Hz to 10^{6} Hz or dc at different temperatures of 30 to 120 °C by using a Novocontrol ALPHA-A high resolution dielectric analyzer.

Figure 3 shows the dc current density of the epoxy composites as a function of filler content in the temperature of 30-120 °C. The results show that the dc current density of the composites doesn't change very much with the addition of either micro BN or nano Alumina. Figure 4 shows the dc current density of the

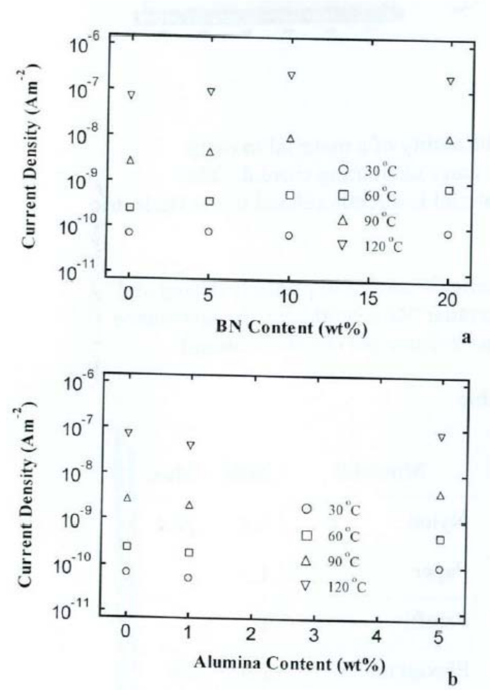

Fig.3. Current densities of epoxy composites at different temperatures. (a) The epoxy composites filled with micro BN; (b) The epoxy composites filled with nano alumina.

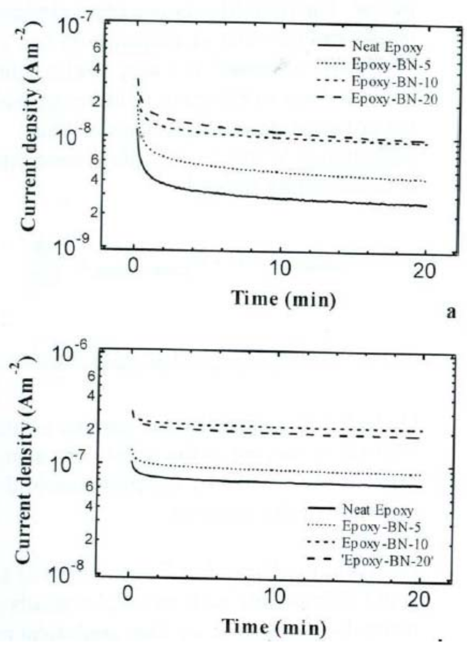

Fig. 4. Current density of the BN filled epoxy composites as a function of the charging time. (a) at 90 °C and (b) at 120 °C.

BN filled epoxy composites as a function of the charging time. The results suggest that the current is suppressed at the higher loading of BN at 120°C. Figure 5 shows the dielectric constant (at 50Hz) of the epoxy composites at a function of BN concentration at different temperatures. The results indicate that the dielectric constant of the epoxy resin increases by 4.5% when loading with 5wt% micro BN, and increases by 5.5% and 7.0% when loading with 10wt% and 20wt% of BN respectively, in the temperature range 30-120 °C. The results also suggest that the temperature dependence of the dielectric constant is relatively weak for all the samples.

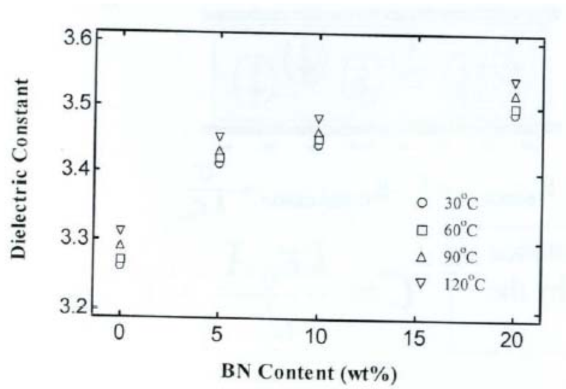

Fig 5. Dielectric constant of the epoxy resin filled with BN at different temperatures.

Typical results for the dielectric constant of these BN filled samples as a function of frequency at 30°C are shown in Figure 6. All samples show that the dielectric permittivity increases with decreasing frequency. This is also found at elevated temperatures.

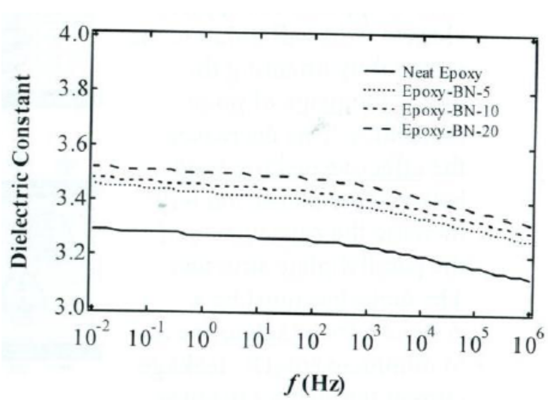

Fig 6. Frequency dependence of the dielectric constant of the BN filled epoxy composites at 30 °C.

III. Thermal Conductivity

The current topic of interest and technical importance in generator business are thermal conductivity of the vapor pressure impregnated (VPI) insulation. For example, in order to improve turbine generator performance, there must be improved thermal conductivity for increased thermal power dissipation capability in the stator slot [10]. Improvements in the thermal conductivity of groundwall insulation systems would be attractive to electrical rotating machine manufacturing in order to gain additional stator design capability, to improve stator performance and gain higher power ratings and more compact designs. Where thermal conductivity enhancement is addressed it is generally achieved by the dispersion of high thermal conductive (HTC) particles, such as boron nitride, silicon carbide and alumina throughout a conventional resin. However, in medium and high-voltage electrical insulation applications, the approaches have been less successful, due to a lack of understanding of the particle size, shape distribution and the interfaces between the particles and the neat resin system.

There is very little reported literature on the improvement of thermal conductivity for high voltage electrical insulation applications. However, the researchers from Gnosys UK and the Engineers from Siemens Power Generation recently had done some work on the thermal conductivity front [6,8] In their study, the overall thermal conductivity of epoxy resin composites with the addition of various inorganic fillers had been well investigated. These individual fillers have high thermal conductivity, and their average sizes span the nano to micro dimension. These fillers were used either singly in the epoxy resin or combined with other fillers to explore the constraints on accessing high thermal conductivity systems. The interfacial behavior and thermal conductivities of insulating epoxy composites and nanocomposites have been investigated.

Figure 7 shows the thermal conductivities at 40 °C of the epoxy/

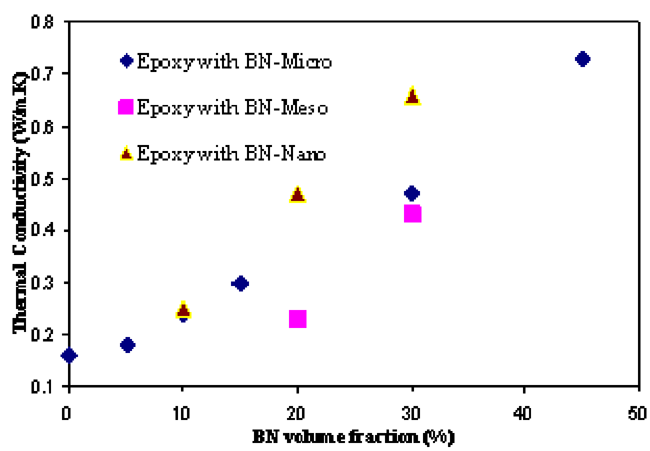

Fig. 7. The thermal conductivities of the epoxy composites filled with BN-Micro, BN-Meso and BN-Nano.

hardener/BN composites filled with BN with different particles sizes. The results from Figure 7 show that the thermal conductivities of all the composites increases with increasing BN concentration in line with typical continuum models predictions. The results also show that there is no big difference between the BN-Micro, BN-Meso and BN-Nano. These results suggest that the size of BN is not necessarily crucial to the thermal conductivity of the epoxy/hardener/filler composites at low to moderate concentrations - the sizes of these BNs are very different.

Another BN with unique micro structure was used for further study. This type of BN called the BN-Aggregate product which has a broader particle size distribution with a hexagonal platelet structure of particle sizes of 5-12µm. This product also has a unique spherical agglomerate of BN crystals while the individual particle has a hexagonal platelet structure. Figure 8 shows the thermal conductivities of the epoxy/BN composites filled with BN-Micro and this special BN-Aggregate.

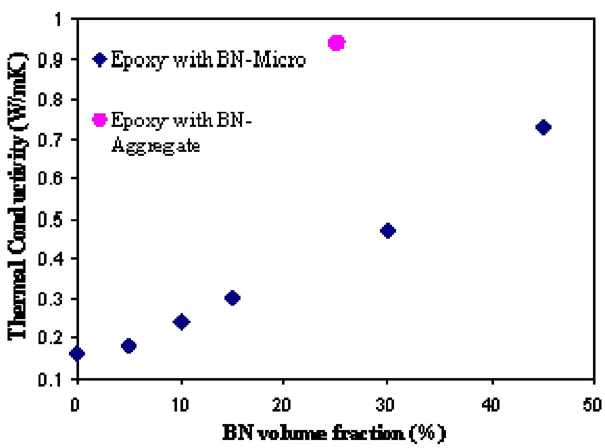

Fig. 8. The thermal conductivities of the epoxy composites filled with micro BN (BN-Micro) and nano BN (BN-Nano)

The results suggest that the BN-Aggregate with the broader hexagonal particle size distribution and spherical agglomerate seems more efficient in enhancing the thermal conductivity of the composites. Comparison of the data in both Figure 7 and Figure 8 show that the BN-Aggregate materials do produce higher thermal conductivities and this is ascribed to their spherical aggregation state which may produce higher three dimensional thermal conductivity in contrast to the single hexagonal platelet BN seen in Figure 1which has a highly anisotropic thermal conductivity.

Some other nano-size ceramic particles (fillers) with relatively high thermal conductivity were also investigated in Dr Han's study. This included nano Aluminum Oxide (α –Alumina), nano Diamond, nano Silicon Carbide (β-SiC) and nano Silicon Nitride (Si_3N_4).

Figure 9 shows the thermal conductivities of the epoxy/hardener/filler composites filled with nano α –Alumina, nano diamond, nano β-SiC and nano amorphous Si_3N_4 at 40°C. The results show that the fillers are not as good as BN in enhancing the thermal conductivity of the epoxy resin composites despite the fillers having comparable or much higher conductivities than BN. There is little difference in the thermal conductivity of the epoxy composites filled with nano α – Alumina, nano diamond, nano β-SiC and nano amorphous Si_3N_4.

Although the thermal conductivities of these nano fillers are reported to be comparable or higher than that of BN, they seem to not work in the DGEBA epoxy resin composites systems. This is in line with our other work on modeling showing that large disparities in mechanical modulus (which translate to the speed of sound, and correlate with the passage of thermal waves – phonons – through the material) cause large thermal contact resistance due to increased phonon scattering resulting from the large mismatch in the high frequency modulus between the filler particle and the resin matrix.

Interfacial mismatch between the filler particle and the resin matrix can also occur as a result of weak or ineffective interfacial bonding.

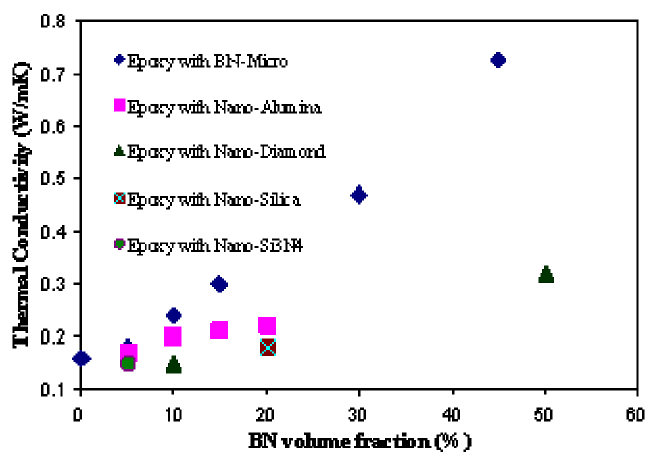

Fig. 9. The thermal conductivities of the epoxy resin composites filled with micro BN, nano alumina, nano diamond, nano SiC and nano amorphous Si_3N_4.

IV. Conclusions

In this paper, the electrical properties and thermal conductivities of epoxy based micro- & nano- composites filled with micro-, meso-, nano- nitrides and oxides and their applications as nanodielectrics to be used as a new class of electrical insulation system for high voltage generator stator use have been well discussed. It was found that several research groups worldwide have now been able to document some significant improvements that potentially can be made especially in the electrical and thermal properties of epoxy resin based nanocomposites through the incorporation of nano-particulates. However, there is still a long way to go in terms of understanding the mechanisms of the enhancement effect in nano dielectric materials and its successful commercial applications in the power generation industry.

ACKNOWLEDGMENT

This work was partly supported by the researchers from Gnosys (UK) scientific company in the UK.

REFERENCES

[1] T. J. Lewis, "Nanometric dilelectrics", IEEE Trans. Dielectr. Electr. Insul., Vol. 1, pp.812-825, 1994.

[2] P.O. Henk, T.W. Kortsen and T. Kvarts, "Increasing the electrical discharge endurance of acid anhydride cured DGEBA epoxy resin by dispersion of nanoparticle silica", High Perf. Polym., Vol. 11, 1999, pp 281-296

[3] M. F. Frechette, M. Trudeau, H. D. Alamdari and S. Boily, " Introductory remarks on nanodielectrics", IEEE Conf. Electr. Insul. Dielectr. Phenomena (CEIDP), PP. 92-99, 2001.

[4] Nelson J.K. and Fothergill J.C., "Internal charge behaviour in nanocomposites", Nanotechnology, Vol. 15, 2004, pp 586-9

[5] J.C. Fothergill, L.A. Dissado and J.K. Nelson, "Nanocomposite materials for dielectric structures", Final report for EPSRC Grant GR/R/ 71788/01, 2002?

[6] Z. Han, B. Wood, H. Herman and G. Stevens, " Thermal properties of composites filled with different fillers", IEEE International Symposium on Electrical Insulation, Vancouver, BC, Canada 9-12 June 2008

[7] K. Chujo, Editor, Advanced technology and application of polymer Nano-Composites, CMC Press, pp. 1-240, 2001 (in Japanese).

[8] C. Zhang, Z. Han and G.C. Stevens, "Effects of micro and nano fillers on electrical and thermal properties of epoxy resins", INSUCON 2006, ICC, Birmingham, England, UK 24-26, May, 2006.

[9] J.K. Nelson, "Overview of nanodielectrics: Insulating materials of the future", IEEE Electrical Insulation Conf. and Electrical Manufacturing expo, Nashville, Tennessee, USA Oct 22-24, 2007

[10] M.L. Miller, F.T.Emery, "Thermal conductivity of high voltage stator coil groundwall insulation,", Electrical Insulation Conference, 1997, and Electrical Manufacturing & Coil Winding Conference., Volume , Issue , 22-25 Sep 1997 Page(s):619 - 622