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# EPOXY ALUMINA NANO-DIELECTRICS: A PROMISING MATERIAL FOR HIGH VOLTAGE INSULATION?

J. Samuel*[1], M. Fu[1] and F. Perrot[1]
[1]ALSTOM Grid Research & Technology, St Leonards Avenue, Stafford, ST17 4LX, UK
*Email: jorice.samuel@alstom.com

**Abstract**: Epoxy-based composites are widely used as medium and high voltage insulators. Conventional micro-composites with alumina and silica micro-fillers have been extensively studied to tailor the properties of neat epoxy resins and reduce their cost. Within the context of a growing interest for nanotechnologies, a large volume of research is published on replacement of micro-fillers by nano-fillers but the results shown are not necessarily consistent notably because the focus has not systematically been on the materials formulation. Herein, the authors prepared vacuum cast epoxy/alumina nano-dielectrics with a particular focus on the processing of the samples. The characterisation of the nano-dielectrics included: mechanical properties, thermal properties and dielectric properties. It was shown that the incorporation of 13 nm alumina nano-fillers yield a strong improvement of the resistance to surface discharges, leading possibly to a larger insulation lifetime. The other properties are not significantly affected. Therefore these results show that despite the growing interest for nanotechnologies and their potential benefits, the results are not as significant as expected and a lot more research must be carried out in the choice of the nano-fillers, their size, their surface treatment and their dispersion.

## 1 INTRODUCTION

Epoxy-based composites are widely used as medium and high voltage insulators. Conventional micro-composites with alumina and silica micro-fillers have been extensively studied and commercialised to tailor the electrical/thermal/mechanical properties of neat epoxy resins and reduce their cost [1]. Within the context of a growing interest for nanotechnologies, the concept of nano-dielectrics has been introduced firstly in 1994 as multi-component devices and systems possessing nanostructures, the presence of which leads to changes in one or several of their dielectric properties. For polymers it implies the replacement of conventional micro-fillers by nano-fillers. Nano-fillers are generally inorganic materials having at least one of their dimensions ranging from 1 to 100 nm and a large surface to volume ratio compared to micro-fillers. Polymer nanocomposites show therefore an enormous interfacial surface area between the nano-fillers and the polymer matrix whose size is critical to the global properties of the composite because it shows properties different from bulk polymer [2]. But, one of the major issues associated with the production of nano-dielectrics is nano-fillers dispersion: nano-fillers have to be properly dispersed to get the optimum properties of nano-dielectrics [3]. Due to their small size, nano-fillers tend to agglomerate and their dispersion in resins is quite difficult [2]. A pre-processing step including nano-fillers surface modification to increase their compatibility and decrease the surface tension is often used [4]. Nano-fillers can be modified by surface functionalization with a silane coupling agent improving the chemical compatibility between the nano-fillers and the matrix and creating tight couplings [1,5,6,7]. Homogeneous dispersion of the powders can also be assisted by shear forces [8], mechanical stirring [5,6,8] and ultrasonic waves [5,6,7]. Alumina micro-fillers have often been used in traditional epoxy composite systems notably to improve the thermal conductivity. Some papers also report the use of alumina nano-fillers. In some cases, alumina nano-fillers are reported to decrease the permittivity (47 nm nano-fillers at a 1wt% loading [4] and 50 nm nano-fillers at a loading from 0.1wt% to 5wt% [9]), to improve the resistance to surface discharges [1], to decrease dielectric losses (30/40 nm nano-fillers at a loading from 0.1 wt% to 5wt% [10]) and to increase the thermal conductivity [7]. Nevertheless, the results are not always consistent, and some permittivity increases are also reported (with 60 nm nano-fillers at a loading of more than 1wt% [5]) as well as unchanged dielectric losses (with 13 nm nano-fillers at a 5wt% loading [6]). This is partly due to the fact that the focus has not always been on materials processing and particularly on nano-fillers dispersion which has to be controlled. A lot of work has still to be carried out on the selection of suitable nano-fillers, their formulation and their dispersion. This work is focussed on epoxy/alumina nanocomposites processed from 13 nm alumina nano-fillers (with and without silane treatment) incorporated at a loading from 0.1wt% to 5wt% with a particular care on material processing. The dielectric, mechanical and thermal properties of the nano-dielectrics are characterised and the results are discussed and compared.

## 2 EXPERIMENTAL

### 2.1 Alumina nano-fillers

Alumina nano-fillers are supplied by Evonik Industries. Two grades are compared:

- Aeroxide Alu C: having a specific surface area of 100 $m^2$/g and an average primary particle size of 13 nm, without surface treatment;
- Aeroxide Alu C 805: having a specific surface area of 100 $m^2$/g and an average primary particle size of 13 nm, with a hydrophobic surface treatment (octylsilane);

### 2.2 Epoxy system

The epoxy studied is a Huntsman system made from the mixture of Araldite MY750 epoxy resin, Aradur HY917 anhydride hardener and DY070 heterocyclic amine accelerator within the proportions 100:90:1 (by weight).

### 2.3 Processing epoxy-alumina nano-dielectrics by vacuum casting

Epoxy/alumina nano-dielectrics are processed by vacuum casting. Two moulds are used: a first mould providing 4 panel samples (dimensions 150 mm x 150 mm x 3 mm) and a second mould giving 16 beam samples (dimensions 150 mm x 10 mm x 4 mm). The process is carefully controlled and reproduced quite faithfully for every set of samples prepared. Nano-fillers are delivered as powders. They are first dried in an oven at 150 deg C for 24 hrs. The resin and hardener are warmed up in an oven for 12 hrs at 60 deg C before being pre-degassed for 10 minutes in an autoclave below 0.3 mm Hg and at 60 deg C (a). Then the nano-powders are dispersed in the resin by mechanical stirring (b-c). When all the powders have been added, an ultrasonic probe (Hielscher 400) is used along with the mechanical stirrer to break the agglomerates and to disperse the powders (d). The hardener is then added under mechanical stirring to the mixture (e). The mixture is degassed in an autoclave for 15 minutes below 0.3 mm Hg and at 60 deg C. The accelerator is then added (2.5 g) and the mixture is stirred gently (f). After a last degassing stage below 0.3 mm Hg and at 60 deg C, the two moulds are poured under vacuum (g). Finally the composites are gelled for 16 hrs at 90 deg C and cured for 2 hrs at 120 deg C. A post curing stage of 4 hrs at 140 deg C and 4 hrs at 160 deg C was added for some of the panel samples.

### 2.4 Characterisations

*2.4.1 Dielectric properties* The permittivity and dielectric losses are measured according to the standard IEC 600250. Electrodes are drawn on panel samples using a DEK 248 screen printer applying an electrically conducting silver paint (Electrodag 976SSHV from Acheson). Then a Schering Bridge is used with a 1kV/mm and 50 Hz AC field at room temperature and room humidity. The DC resistivity is assessed using the same electrodes. It is calculated from the current intensity measured with a Keithley 602 solid-state electrometer according to the standard IEC 60093. Measurements are taken at room temperature and room humidity at an applied DC voltage of 1.7 kV/mm. The resistance to surface discharges is characterised according to the standard IEC 60343. Corona discharges are generated by the continuous application of a 10 kV AC voltage to cylindrical aluminium electrodes. A 100 µm air gap is set between the sample and the electrode and to maintain a constant discharge activity, dry air is blown towards the surface to remove ozone (at 0.5 l/min). The measured discharge activity at this voltage is around 4000 pC. The depth of erosion is regularly measured with a portable profilometer.

*2.4.2 Thermal properties* The glass transition temperature is measured by two methods: DSC (differential scanning calorimetry) and TMA (thermo-mechanical analysis). DSC measurements are carried out on 3-4 samples (around 80 mg) for each formulation (cut from both panel and beam samples), using a Perkin-Elmer DSC7 instrument between 20 ºC and 250 ºC at a temperature rate of 20 ºC/min. TMA measurements are carried out on one beam (50 mm x 5 mm x 3 mm) for each formulation, using a Netzsche dilatometer instrument between 25 ºC and 200 ºC at a temperature rate of 3 ºC/min. The Netzsche dilatometer also gives a value of the thermal expansion coefficient. The thermal conductivity is characterised using a Lee's disc apparatus between 20 ºC and 100 ºC on a disc of 50 mm diameter cut from the panel samples.

*2.4.3 Mechanical properties* Flexural properties are measured on beam samples using a Hounsfield 50 kN apparatus following the British Standard ISO 178. The test is carried out at 2mm/min and 10 to 12 samples are characterised per batch. The flexural modulus is calculated from the strain-stress curves obtained.

## 3 RESULTS

### 3.1 Processing conditions

The nano-dielectrics prepared have been fully characterised in terms of mechanical, thermal and dielectric properties. However, before describing the results, Table 1 shows the record of manufacture for the samples processed. It is indeed important to make sure that the nanocomposites are processed at similar temperatures and with the same dispersing techniques so that the differences observed are only due to the incorporation of nano-fillers and not to process variations. The only variation in the process is for step b: nano-fillers are dispersed in the resin at a constant addition rate (500 mg per minute), so typically it took 10 minutes to disperse 5 g of powders. Apart from that, the dispersion tools used (mechanical stirrer and ultrasonic processor) are the same for every formulation processed and they are always used at the same intensity and for the same duration. Heat treatments are fairly similar, so temperature variations are quite low from a formulation to another: typically, after step c, the average temperature recorded is 39.6 °C and the average deviation to this temperature is 4.1%; after step d, the average temperature is 82.3 °C and the average deviation is 3.7%. So at crucial steps for nano-fillers dispersion, the processing conditions are very similar: the dispersion state is controlled and should be quite reproducible. However, when the filler loading increases, it would have been better to increase the ultrasonic mixing duration too but as the temperature rapidly increased (up to 90 °C after 5 minutes), it was decided not to proceed. So it might be possible that at the highest loading levels, the powders are not well dispersed.

## 3.2 Dielectric properties

*3.2.1 Permittivity* It is an important parameter as it is used to control the AC electric field distribution in an insulator. The permittivity of post cured samples is measured on 2-3 samples per formulation for each formulation (Figure 1). For untreated and silane treated nano-fillers, marginal variations are observed (within margins of error). Besides, permittivity variations observed for samples from different batches but with the same loading level (5wt%) are rather low: 2% for untreated nano-fillers and 1.3% for silane treated nano-fillers. These results confirm that the processing methods were fairly similar even at the highest filler loading and that the nano-dielectrics prepared have rather consistent dielectric properties. The conclusion here is that the permittivity at 50 Hz is not seriously affected by the incorporation of a quantity of 0.1wt% to 5wt% of both untreated and silane treated 13 nm alumina nano-fillers.

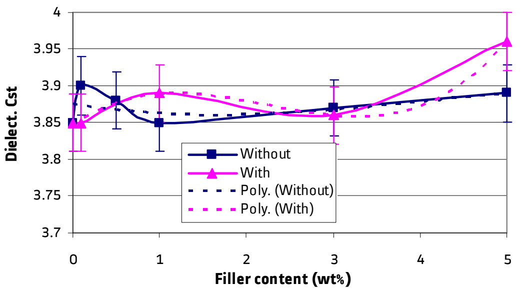

**Figure 1:** Permittivity against filler content

*3.2.2 Dielectric losses* They give an indication of the resistive leakage current circulating through the volume of an insulator. It is therefore a value representing the quality of the insulation. Dielectric losses (tan delta) of post cured samples are measured on 2-3 samples per formulation for each formulation (Figure 2). Among the range of filler loadings studied and for both grades, there is no significant variation of the dielectric losses. So in that case, nanostructuration has no effect on the dielectric losses measured at 50 Hz. Similar conclusions have been reported elsewhere [6].

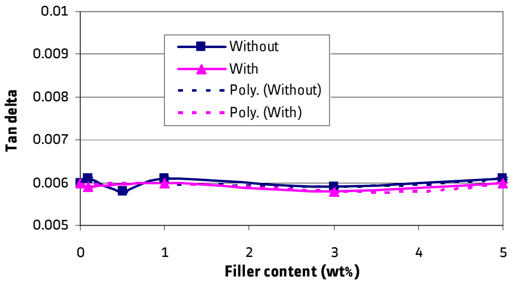

**Figure 2:** Dielectric losses against filler content

*3.2.3 DC Volume Resistivity* It also gives an indication of the leakage current circulating through the volume of the insulator. It is therefore a value representing the quality of the insulation. DC Resistivity of post cured samples is measured on 2-3 samples per formulation for each formulation (Figure 3).

| Temperature in deg C | Neat | 0.1wt% | 0.1% silane T | 0.5wt% | 1wt% - 2 | 1wt% silane T 2 |
|---|---|---|---|---|---|---|
| Before nano-addition (a) | 57 | 50 | 52 | 55 | 49 | 55 |
| After nano-addition (b) | 45 |  | 47 |  | 40 |  |
| After mechanical stirring (c) | 41 | 42 | 42 | 43 | 38 | 39 |
| After ultrasonic processing (d) | 81 | 75 | 82 | 76 | 82 | 81 |
| After hardener addition (e) | 67 |  |  | 56 | 59 | 58 |
| After accelerator addition (f) | 60 | 47 | 55 | 56 | 57 | 56 |
| Autoclave temperature @ end of process (g) | 70 | 68 | 69 | 69 | 61 | 70 |

| Temperature in deg C | 3wt% | 3wt% silane T2 | 5wt% | 5wt%2 | 5wt% silane T | 5wt% silane T3 |
|---|---|---|---|---|---|---|
| Before nano-addition (a) | 56 | 54 | 56 | 62 | 57 | 58 |
| After nano-addition (b) | 42 | 29 | 39 | 41 | 38 | 36 |
| After mechanical stirring (c) | 40 | 38 | 39 | 39 | 38 | 36 |
| After ultrasonic processing (d) | 88 | 84 | 86 | 82 | 90 | 81 |
| After hardener addition (e) | 61 | 57 | 59 | 60 | 57 | 54 |
| After accelerator addition (f) | 59 | 55 | 55 | 58 | 54 | 54 |
| Autoclave temperature @ end of process (g) | 67 | 57 | 68 | 72 | 66 | 61 |

**Table 1:** Record of manufacture (temperature) for nanocomposites processing

All the samples are characterised on the same day after having been conditioned for 24 hrs at 100 deg C and cooled down 6 hrs at room temperature in controlled atmosphere. When nano-fillers are silane treated, DC resistivity is not significantly affected at any filler loading even though it is marginally higher compared to the neat resin. When nano-fillers are not pre-treated, variations are more significant: the resistivity is increased at every filler loading and goes through a maximum for a 1wt% loading. It is reported in the literature [11] that the resistivity should first decrease with nano-fillers incorporation due to the introduction of free ions and then increase at higher loadings (between 1 and 5wt%), due to the increased fraction of immobile polymer layers acting as charge traps. However this behaviour is restricted to nano-dielectrics showing a homogeneous dispersion. Besides, the variations seen herein are quite low and the resistivity values are all in the same order of magnitude. So, the incorporation of nano-fillers does not decrease DC resistivity: it either remains constant or is slightly improved depending on nano-fillers surface treatment.

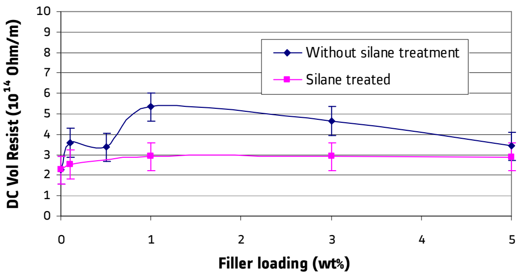

**Figure 3:** DC Resistivity against filler content

*3.2.4 Resistance to surface discharges* It is linked to ageing of the insulation under abnormal high stress conditions: a better resistance improves insulators lifetime. It has been measured for some samples over 900 hours. Figure 4 shows the evolution of the erosion depth for nano-dielectrics filled with untreated alumina nano-fillers. After 300 hours, there is already a large difference between the neat resin and nano-dielectrics prepared with a loading in alumina nano-fillers between 1wt% and 5wt%. Nano-fillers addition strongly improves the resistance to surface discharge. Erosion rates between 0 and 300 hours have been compared for all the samples and are shown in Figure 5. For untreated nano-fillers, there is a strong improvement of the resistance to surface discharges with a 1wt% loading, then the value at 3wt% is quite similar and finally at 5wt%, it is improved again. For silane treated nano-fillers, the improvement starts at 0.1wt%, it is then stable up to 3wt% and it increases again at 5wt%.

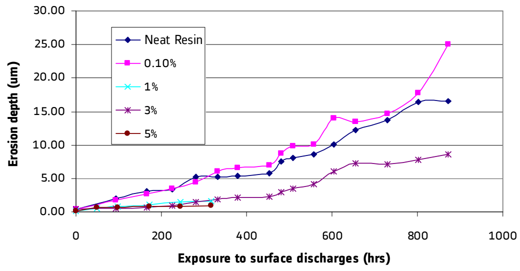

**Figure 4:** Evolution of the erosion depth of nano-dielectrics filled with untreated nano-fillers

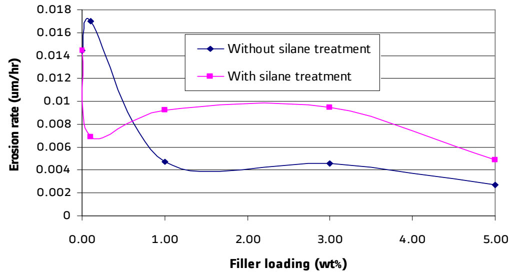

**Figure 5:** Erosion rate of nano-dielectrics against filler content

Although the erosion depth measurement with the profilometer is not accurate, the differences observed are significant enough to conclude that the addition of both grades of alumina nano-fillers largely improve the resistance to surface discharges. A similar result has already been reported elsewhere [1]. One possible explanation is the segmentation of the polymer matrix in small areas containing nano-fillers with intrinsic higher resistance to PD, and the strong coupling with the surrounding polymer. In this study, untreated nano-fillers perform better than silane-treated nano-fillers. There is neither evidence of a strong bonding between nano-fillers and the polymer matrix, nor adequate dispersion of nano-fillers so there is still room for improvements. This is therefore a promising result leading to a possible improvement of insulators lifetime.

## 3.3 Thermal properties

*3.3.1 Glass transition temperature* It is important as it sets the upper limit temperature at which the material can be used. It shows a higher value when measured by DSC compared to TMA. However, we will only consider the variations due to the incorporation of nano-fillers. Particularly it can be seen on Figures 6 and 7 that the variations observed by both methods are quite similar. For untreated nano-fillers, Tg is rather constant and does not seem to be influenced by nanostructuration. For silane treated nano-fillers the behaviour is more complex to interpret: the values are similar to the neat resin except for the 3wt% sample which shows a lower Tg value.

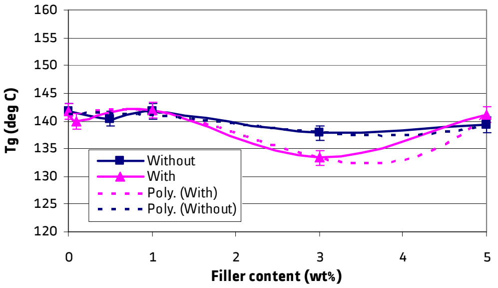

**Figure 6:** Evolution of Tg measured by DSC against filler content

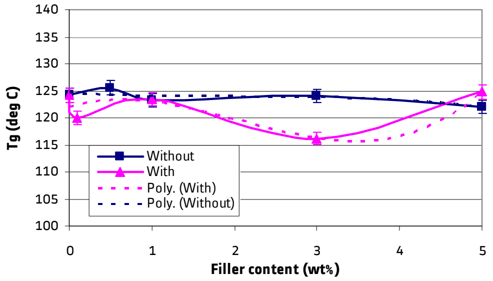

**Figure 7:** Evolution of Tg measured by TMA against filler content

Tg variations due to nanostructuration are not well established in the literature although a decrease in the Tg value has already been reported after the incorporation of 45 nm alumina nano-fillers [12]. In some cases, it has been assumed that an enhanced polymer chain mobility due to the incorporation of nano-fillers and to weak bonds between the nano-fillers and the matrix lead to a decrease in the Tg value whereas, at higher loadings and when there is a strong bond, the number of immobile polymer chains increases and so does the Tg value. But it is strongly dependent upon nano-fillers dispersion [11]. Herein, Tg is slightly decreased when untreated nano-fillers are used, so they might not strongly bond to the matrix. When silane treated nano-fillers are used, Tg is decreased too and more significantly at a 3wt% loading, so the silane treatment used is not suitable for epoxy systems and does not create strong chemical bonds between nano-fillers and the matrix.

*3.3.2. Thermal expansion* It has to be considered as the insulating material is often in contact with conducting metals having a lower thermal expansion, so the thermal expansion of the insulator has to be decreased to prevent a thermal mismatch between both materials. The coefficient of thermal expansion has been estimated for every formulation at 50 ºC (Figure 8). The value obtained for the neat resin is consistent with values reported in the literature [8] and it does not seem to be influenced by the addition of nano-fillers, even at the highest loading studied (5wt%). So, herein nanostructuration has no impact on the thermal expansion.

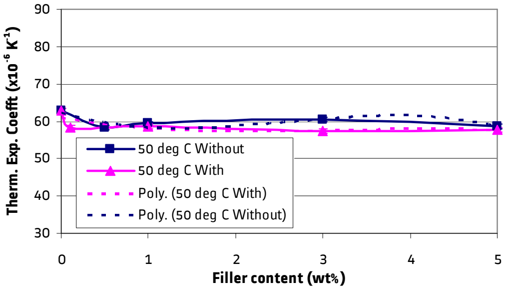

**Figure 8:** Evolution of thermal expansion coefficient against filler content

*3.3.3 Thermal conductivity* It has to be high enough to allow better heat dissipation. Improving the thermal conductivity of a dielectric is an objective when designing insulating systems, particularly to decrease the size of the insulating layer or increase the power density of the electrical equipment. The thermal conductivity value measured by the Lee's disc method is fairly similar to values traditionally reported for epoxy systems (Figure 9) [7].

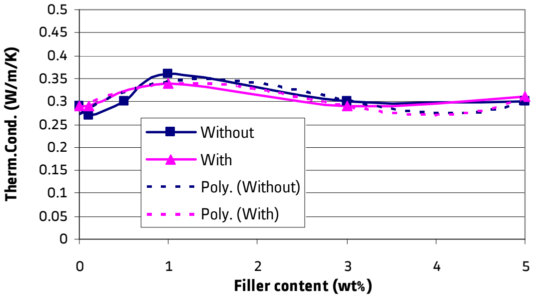

**Figure 9:** Evolution of Thermal conductivity against filler content

Here again the effect of the addition of 13 nm alumina nano-fillers is not significant and is within the margins of error of the measurement. It seems that there is neither collaborative effect nor percolation between the nano-fillers, otherwise thermal conductivity would have been increased.

### 3.4 Mechanical properties

The flexural modulus is calculated from strain-stress curves obtained during the flexural tests. For each formulation prepared 10 to 12 samples are measured and the value represented is an average value (Figure 10). The flexural modulus value of the neat epoxy resin is around 3.2 GPa. It shows no significant variation when silane treated nano-fillers are incorporated, even at a 5wt% loading whereas for untreated nano-fillers, it gradually increases from 1wt% to 5wt% and the value obtained for the 5wt% loading is around 3.5 which is higher than for the neat resin. So when untreated nano-fillers are used, the flexural properties at high contents can be improved.

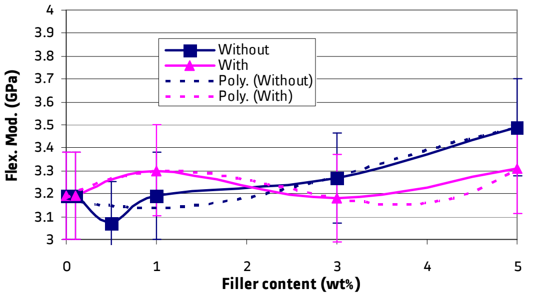

**Figure 10:** Evolution of flexural modulus against filler content

## 4 CONCLUSION

Epoxy/alumina nano-dielectrics have been prepared using 13 nm alumina nano-fillers. A full set of electrical, thermal and mechanical characterisations has been carried out. Particularly, it is evidenced that the resistance to surface discharges is improved, leading to insulators with a potential longer lifetime. It is nevertheless important to notice that the other properties (permittivity, DC resistivity, dielectric losses, thermal conductivity, thermal expansion, Tg and flexural modulus) are either constant or slightly improved as well. Particularly untreated nano-fillers perform slightly better than silane treated nano-fillers in terms of Tg, DC volume resistivity, resistance to surface discharges and flexural modulus, meaning that the silane treatment used may not be adapted to the epoxy resin studied and led to a weaker interface. The interface has therefore to be carefully tailored to get the optimum properties of the nano-dielectrics. These first results are nevertheless promising and show that materials processing is important to get the full potential of nano-dielectrics.

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