

# COMPARISON OF THE DIELECTRIC RESPONSE OF ALUMINA-EPOXY COMPOSITES WITH NANO- AND CONVENTIONAL SIZED FILLER

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**Abstract:** This paper looks at the differences in dielectric response between epoxy resin composites with conventional and nanoscale alumina filler. Host material, namely bisphenol-A epoxy resin, is the same for all samples. Preparation of the samples is described in detail. Both filler types are treated in similar fashion to ensure comparability of the results. An even distribution of the alumina in case of the nanoscale filler was validated by means of transmission electron microscopy. It is shown by means of dielectric spectroscopy how the particle size and preparation influence the material properties. Measurements were performed in a broad frequency range between 0.01 and 10 MHz, for temperatures between -20C and the glass transition temperature of the host material close to 120C. Possible explanations for the witnessed behavior are presented and the contributing factors discussed.

## 1. INTRODUCTION

Ever since Lewis published *Nanometric Dielectrics* in 1994 [1], the amount of publications regarding nanodielectrics for electrical engineering increased constantly. The effects witnessed in nanocomposites are considered to be due to a number of contributing factors. These are including size of the particles, distribution or surface treatment, as shown in various publications e.g. [2]. Comparisons with conventional filler material have been made on several occasions, but often the related chemistry has only been described in detail for the nanoscale filler. It has been shown that the surface functionalization of nanoparticles has considerable impact on the dielectric behavior (e.g. in [2]). The question of how much the particle preparation and not the size of the filler material influence the properties is unsolved. In the course of this work we take a look at conventional sized and nanoscale  $\text{Al}_2\text{O}_3$ .

## 2. SAMPLES

### 2.1. Material

The samples discussed in this paper are all based on the same bisphenol-A type epoxy resin system (ER) consisting of resin CY231 and anhydrite hardener HY925 from Huntsman. The  $\text{Al}_2\text{O}_3$ -nanofiller with average diameter of 50nm was obtained from Sigma Aldrich. The conventional filler for comparison has a average particle size of  $4\mu\text{m}$  and was obtained from Albemarle. For functionalization of  $\text{Al}_2\text{O}_3$   $\gamma$ -Glycidoxypropyltrimethoxysilane (GPS) from Sigma Aldrich was used. The fillgrades were 0.5%, 2%, 5% and 10% wt. for nanoscale filler, 5% and 10% for conventional sized filler (see Table 1). Unfilled ER samples were used for comparison and reference measurement.

**Table 1.** Samples used.

Filler	av. size	fillgrade	GPS	Sample name
none	-	-	no	neat ER
$\text{Al}_2\text{O}_3$	50nm	0.5%	yes	nano-0.5
$\text{Al}_2\text{O}_3$	50nm	2%	yes	nano-2
$\text{Al}_2\text{O}_3$	50nm	5%	yes	nano-5
$\text{Al}_2\text{O}_3$	50nm	10%	yes	nano-10
$\text{Al}_2\text{O}_3$	$4\mu\text{m}$	5%	no	unmod-5
$\text{Al}_2\text{O}_3$	$4\mu\text{m}$	10%	no	unmod-10
$\text{Al}_2\text{O}_3$	$4\mu\text{m}$	5%	yes	mod-5
$\text{Al}_2\text{O}_3$	$4\mu\text{m}$	5%	yes	mod-10

### 2.2. Sample preparation

The samples with nanoscale filler and one batch of conventional sized filler for comparison were fabricated using in-situ polymerization for surface functionalized  $\text{Al}_2\text{O}_3$ . The as-received particles were dispersed in 96% ethanol by means of ultrasonication at room temperature. The pH-value of the solution was adjusted with formic acid to 4 in case of the nanofiller. This was done to reach a higher  $\zeta$ -potential for the  $\text{Al}_2\text{O}_3$  particles, to prevent agglomerates and achieve a solution with finely dispersed particles. Then the GPS was added and the suspension underwent further sonification to allow hydrolysis. Resin CY231 was added and the obtained solution stirred with a high shear mixer for typically 15 minutes. Afterwards the mixture was put into a vacuum oven at  $90^\circ\text{C}$  to evaporate the solvent. Due to trapping of the ethanol molecules in the resin this step took a considerable amount of time. The weight of the mixture was controlled before introducing the curing agent, to ensure that the solvent evaporated completely. After addition of the curing agent, the resulting mixture was stirred with a high shear mixer and degassed for typically one hour. To see the influence of the surface functionalization, one batch of

samples has been created with GPS treated conventional filler. The surface functionalization was similar to the processing for the nanoscale filler. For samples with conventional  $\text{Al}_2\text{O}_3$  that were not functionalized, the as-received filler was simply stirred with resin and hardener by means of high shear mixing. Afterwards the mixture was degassed. All samples cured at  $140^\circ\text{C}$  for 16 hours in Al-molds and were postcured for 2 days at  $120^\circ\text{C}$ . To see the influence of the curing time one batch of samples has been cured for 3 hours at  $140^\circ\text{C}$  and postcured for 2 days at  $120^\circ\text{C}$ .

### 2.3. Validation of particle dispersion

The quality of the dispersion was validated for samples with nanoscale  $\text{Al}_2\text{O}_3$ -filler by means of transmission electron microscopy (TEM). Details can be found in [3]. TEM indicates that the nano-alumina-ER-composites show good dispersion, especially in samples with 2% per weight. In samples with 0.5 and 5wt.% some agglomerates of up to 100nm could be found.

## 3. DIELECTRIC SPECTROSCOPY

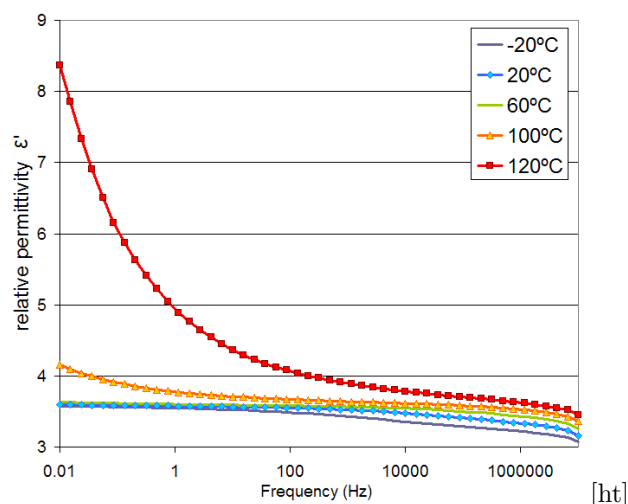
The complex permittivity was measured in the frequency range of 0.01 Hz to 10 MHz using a broad band dielectric spectrometer from Novocontrol with a ZGS Alpha active cell and automatic temperature control by a Quatro cryosystem with a precision of  $0.01^\circ\text{C}$ . This setup measures the complex permittivity  $\varepsilon$  (see eq. 1) as a function of frequency and temperature. The real part  $\varepsilon'$  is known as the relative permittivity  $\varepsilon_r$ . The imaginary part  $\varepsilon''$  is attributed to the dielectric losses in the material. These two parts are connected, a drop of the  $\varepsilon'$  value shows as a peak in the  $\varepsilon''$ -spectrum. Aluminum electrodes were sputtered on the surface of the samples, to ensure good contact between the electrodes of the active cell and the sample. Certain processes show up at different frequencies and temperatures. To get the whole picture, we tested the samples from  $-20^\circ\text{C}$  until  $120^\circ\text{C}$ , which is close to the glass transition temperature. Since humidity can influence the measured values, the samples were dried in an oven at  $120^\circ\text{C}$  for two days before measurement and kept under nitrogen-atmosphere for the duration of the measurement. The drying process also served as post-curing.

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad (1)$$

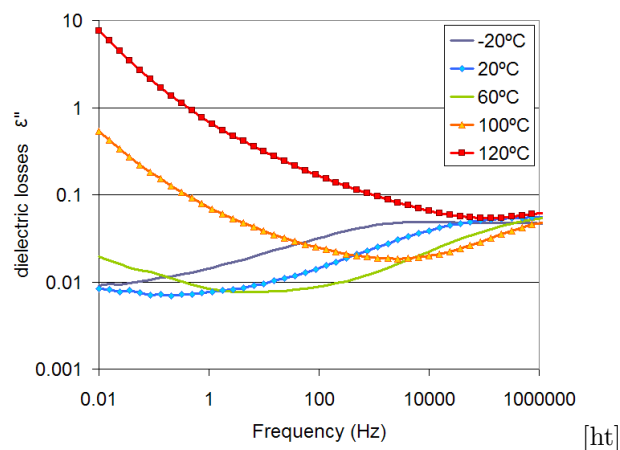
## 4. MEASUREMENT RESULTS

### 4.1. Neat epoxy resin

The base ER shows normal behavior with an  $\alpha$ -relaxation peak at the glass transition temperature, which can be seen at low frequencies for tempera-



**Figure 1.** Relative permittivity for neat ER as a function of frequency.



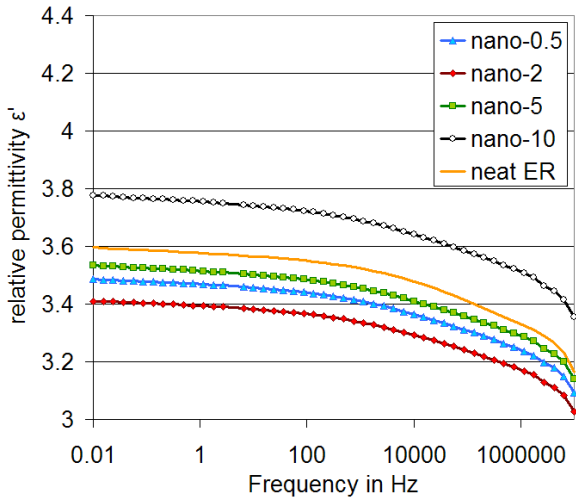
**Figure 2.** Dielectric losses for neat ER as a function of frequency.

tures of  $80^\circ\text{C}$  and above. See figure 1 for relative permittivity, figure 2 for dielectric loss spectrum. We also see peak in the spectrum of the epoxy that moves to higher frequencies with increasing temperature. We attribute this to a  $\beta$ -relaxation process that can be seen at 1 kHz for  $-20^\circ\text{C}$  and 100 kHz for  $20^\circ\text{C}$ .

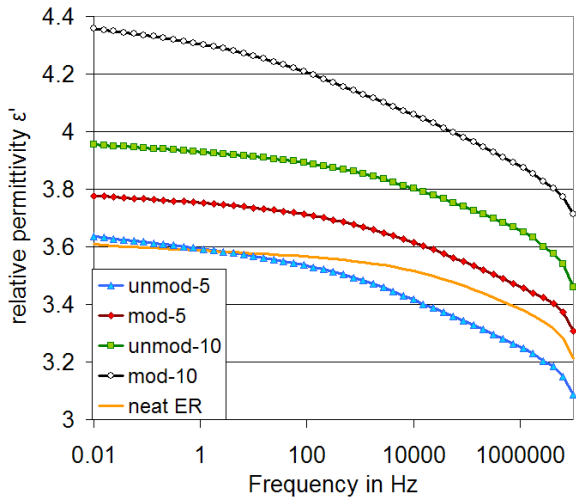
### 4.2. $\text{Al}_2\text{O}_3$ -ER composites

The relative permittivity of  $\text{Al}_2\text{O}_3$ -ER composites with nanoscale filler is in most cases lower than the base ER (see Fig. 3). Only exception being the 10wt.% nanocomposite which shows an increase of the permittivity by 5%. The dielectric loss spectrum looks very similar to the spectrum of neat ER. Differences can be found in the low frequency region. The losses for temperatures of  $60^\circ\text{C}$  and higher are increased for the nano-10 sample, while they were decreased for the other samples with nanoscale filler.

Figure 4 shows values for samples with both modified



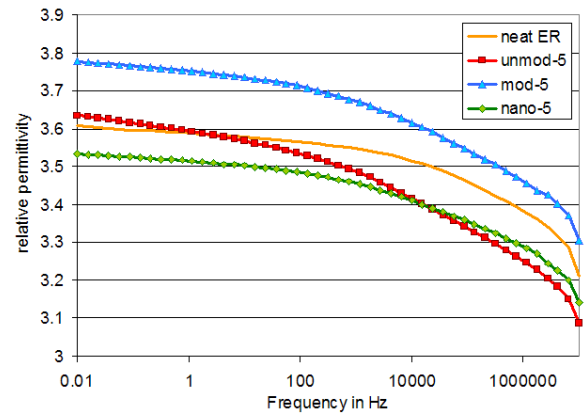
**Figure 3.** Relative permittivity at 20°C for nanocomposites compared to neat ER as a function of frequency.



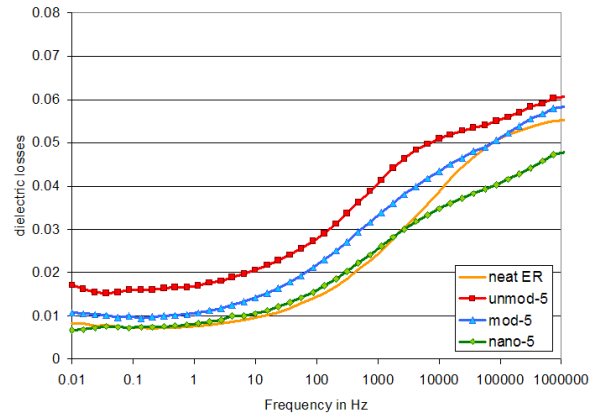
**Figure 4.** Relative permittivity at 20°C for samples with conventional filler (both modified and unmodified) compared to neat ER as a function of frequency.

and unmodified conventional sized filler compared to neat ER. It is apparent that permittivity values for samples with modified particles are higher than with unmodified. Sample unmod-5 exhibits similar values for  $\epsilon'$  up to 100 Hz. Above this frequency the permittivity is lower than in the base epoxy and above 10 kHz even lower than for samples with nanoscale filler (see Fig. 5). The curve for mod-5 looks almost identical, except that the values are on average 0.2 higher than for unmod-5. Samples with 10wt.% see further increase in permittivity. For example at 50 Hz we see an increase of the permittivity by 9% for unmod-10, while the increase for mod-10 is 19%.

Figure 6 shows a comparison of the dielectric losses of samples with 5wt.% for 20° as a function of frequency. We can see that unmod-5 shows the highest losses while values for mod-5 and nano-5 are rel-



**Figure 5.** Relative permittivity at 20°C for composites with 5wt.% compared to neat ER as a function of frequency.

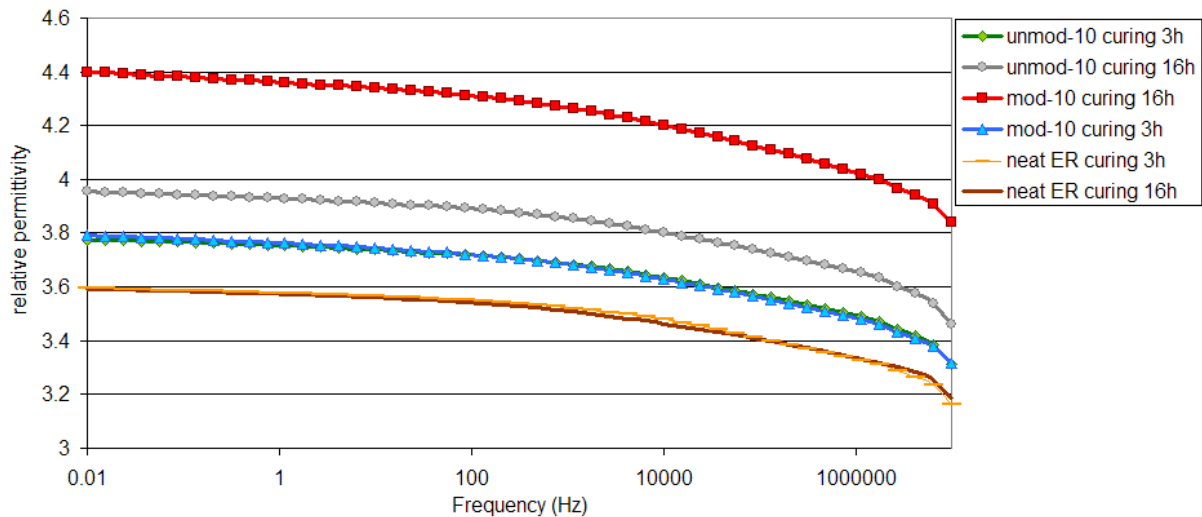


**Figure 6.** Dielectric losses at 20°C for composites with 5wt.% compared to neat ER as a function of frequency.

atively close together for frequencies below 50 Hz. above 1 kHz nano-5 shows the lowest losses, while  $\epsilon''$  values for mod-5, unmod-5 and neat ER samples approximate. For samples with 10wt.% the behavior is different. While nano-10, unmod-10 and neat ER have similar values there is an increase for mod-10.

#### 4.3. Influence of the curing time on $\text{Al}_2\text{O}_3$ -ER composites

Measurements above have been conducted on samples with curing times of 16 hours at 140°C. We also created samples with curing time of 3 hours for comparison. Figure 7 shows the influence of the curing time on samples with microscale filler and fillgrade of 10wt.% compared to neat ER. We can witness an increase of the relative permittivity in samples with longer curing time albeit we see no difference on the base epoxy. Also we see that the measured values for modified and unmodified particles are overlapping and almost identical for samples that have been cured for 3 hours.



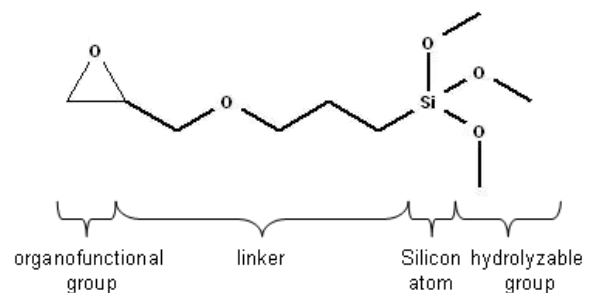
**Figure 7.** Influence of the curing time on the dielectric permittivity at 20°C for composites with 10wt.% compared to neat ER as a function of frequency.

## 5. DISCUSSION

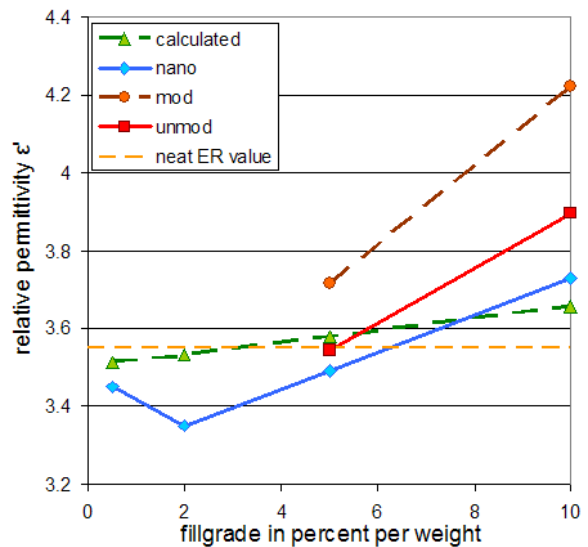
One of the things many publications about nanodielectrics share are comparisons with conventional sized filler material, thus sizes in the micrometer range. In most cases the chemistry involved in creating the samples with microscale filler is neglected. It has been shown that surface functionalization of nanoparticles is crucial for the properties of nanocomposites (as in e.g. [2]), but the influence of surface functionalization on micron sized filler is not taken into account. This publication shows how changes of particle preparation or curing time can alter the dielectric properties of the overall composite. In light of these results the comparisons between nano- and microscale filler without detailed knowledge of chemical processes involved have to be re-evaluated.

In earlier work [3] we suggested that the surface functionalization of alumina with GPS changes the structure of the material. The hydrolyzable group of the used GPS (see Fig. 8) connects to OH-groups on the particle surface, while the organofunctional group is an epoxy group and will be connected to bisphenol-A chains of the resin by the curing agent. The curing agent HY925 can only connect two epoxy groups, thus the base resin is linear. GPS modified particles sport many epoxy groups, can therefore act as nodes for chain growth cross-linking the polymer. The number of possible epoxy groups on the particle surfaces is of course correlated with the interfacial area between filler and matrix material. Since nanoscale filler have a larger interfacial area for the same weight percentage as microscale filler the structural changes due to GPS treatment might be more distinct in nanodielectrics.

The dielectric spectrum of the base ER is as ex-



**Figure 8.** Chemical structure of the GPS used.



**Figure 9.** Measurement values for relative permittivity at 20°C compared to calculated values as a function of fillgrade.

pected. It indicates a large peak for frequencies below 10 Hz around 120°C, which we attribute to an  $\alpha$ -relaxation process at the glass transition temper-

ature. We also see a peak that moves to higher frequencies with increasing temperature. It can be seen at 1 kHz for  $-20^{\circ}\text{C}$  and 100 kHz for  $20^{\circ}\text{C}$ . We attribute this peak to a  $\beta$ -relaxation process. Relative permittivity for  $20^{\circ}\text{C}$  and 50 Hz is 3.55. Values for nanocomposites range between 3.35 and 3.73, being 5% lower respectively higher than the base ER. Modified microscale fillers see a permittivity increase of up to 19% for 10wt.% fillgrade. When we compare the results for the relative permittivity we notice a drop for three of the nanocomposites (see Fig. 9). We also see a reduction for samples with 5wt.% unmodified conventional filler for frequencies above 1 kHz.

The dielectric constant for  $\text{Al}_2\text{O}_3$  is between 9.5 and 10 depending on structure [4]. There are two main groups of theoretical approaches to the problem of composite permittivities: effective medium (or mean field) theory and integral methods [5]. The former group utilizes average fields or polarizabilities and induced dipole moments, the latter uses low concentration formulae and integrate them to higher concentration. Factors taken into account by conventional mixture rules are volume content of the filler, inhomogeneities, particle shape, orientation and distribution as in e.g. [6]. According to conventional mixture rules for composites the permittivity of the compound should be between the value of filler and matrix material. We used the Looyenga formula for an approximation of the relative permittivity (see Eq. 2 with  $v_x$  being volume fractions of the materials involved). The comparison of calculated and measurement results can be seen in Fig. 9.

$$\bar{\epsilon}^{\frac{1}{3}} = v_1\epsilon_1^{\frac{1}{3}} + v_2\epsilon_2^{\frac{1}{3}} \quad (2)$$

Factors that are not taken into account by laws of mixture are particle size, surface treatment or structural changes in the material due to the introduction of the filler material. We showed how much measured permittivity values can differ due to variations of particle size or surface treatment. Taking these factors into account makes proper use of a rule of mixture for nanocomposites a complex task and there are more uncertainties that have not been addressed here. The approximated values are too high for nanoscale  $\text{Al}_2\text{O}_3$  and too low for modified micron sized filler. We also witnessed a considerable increase of the permittivity for samples which were produced from the same batch but were cured longer (Fig. 7).

## 6. CONCLUSION

The relative permittivity and dielectric losses of binary composite systems have been determined by means of dielectric spectroscopy. Aluminum oxide particles of two different sizes (50nm and  $4\mu\text{m}$ ) have been used. To see the influence of the interface

between matrix material and filler, silane coupling agent has been used for samples with nanoscale filler and half of the samples with micron sized filler. The influence of the curing time has also been investigated for filler in the microscale. It could be shown that permittivity of alumina filled epoxy samples with microscale filler can be altered by use of surface functionalization. Measured values for the relative permittivity have been compared to calculated values according to mixture rules for composites. Several reasons could be identified why the values calculated with conventional theory do not agree with the measured values. Main problem with current mixing theories is that they do not take into account the ratio between particle size and interfacial zone or the quality of the interface. It is very difficult to take into account how much the structure of the base polymer changes due to the introduction of surface functionalized nanoparticles. These factors make it very complex to use a rule of mixture for polymer based nanocomposites or composite systems with improved interfaces due to surface functionalization of the filler material.

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