The Effect of Interphase Structures in Nanodielectrics

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Keywords: nanodielectrics, nanocomposites, interphase, nanoparticles

Nanometric dielectrics promise significantly improved material properties for high voltage insulation. It is remarkable, that the improvements already occur at very low filler concentrations of 1-10 wt. % according to published results. As an explanation for the improvements it is assumed that the interfaces between filler particle and matrix material have a dominant influence on the material properties. The polymer area around each filler particle (interphase) should be considered as a layer with a certain thickness. In the interphase the polymer chains are chemically and/or physically bond to the particle surface causing a polymer structure different from the structure of the remaining amorphous matrix material. Therefore the properties of the interphase can differ from the properties of the matrix material.

The interphase fraction is estimated by using a simplified model, depending on filler diameter $d$, filler concentration $V_p$, and interphase thickness $i$. The following assumptions for the filler particles are made:

1. All particles are spherical surrounded in an interphase of constant thickness $i$.
2. All particles have the same diameter $d$.
3. The particles are homogenously dispersed in the matrix material.

If the particles are dispersed homogeneously, one can define a basic element (Fig. 1), which is bordered by the centres of eight particles at each corner of the cube. The distance between the centres of neighbouring particles is $a_0$. Furthermore is assumed, that one particle is located in the centre of the cube, having the same distance to its eight neighbours.

The model shows that the interphase fraction has a distinct maximum of the interphase fraction at very small particle diameters and small filler concentrations (Fig. 2). Different parameters like the particle size, the particle shape, the dispersion of the filler particles, the interphase thickness and structure can influence the interphase fraction significantly.

For particles with a diameter of 10 nm at a filler concentration of 10 vol.% the interphase fraction is approximately 70 vol.% for example. It can be assumed, that the interphase properties dominate the material properties due to its high fraction. At high filler concentrations the interphase fraction is decreasing. If the filler fraction is high enough, the filler properties will have a dominant influence on the material properties. Hence, the nano effect will occur at very small particle diameters and relatively small filler concentrations. Only in this combination interphase fractions $> 40$ vol.% can be achieved.

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Fig. 1. Basic element with diagonal $\sqrt{2}a_0$

Fig. 2. (a) Calculation of the interphase fraction with an interphase thickness of $i = 5$ nm and variable diameter $d$ of filler particle (b) Filler fraction, interphase fraction and fraction of remaining polymer at a particle diameter of $d = 20$ nm and an interphase thickness of $i = 5$ nm.
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The interface between the polymer and the filler particles influences the properties of dielectric materials. To understand how interfaces act, they should be considered as layers rather than interfaces. Therefore the term interphase is more appropriate for the polymer layer around a filler particle where the polymer chains are chemically and/or physically bound to the particle surface.

The interphase is characterized by an ordered polymer structure around the particles. This paper discusses the influence of the ordered polymer structure around the particles on the polymer properties with regard to explain the effect of nano particles on material properties.

In this paper also a model is given how to estimate the maximum interphase fraction depending on particle diameter and interphase thickness. It is postulated that the most significant results can be achieved at this maximum.

Keywords: nanodielectrics, nanocomposites, interphase, nanoparticles

1. Introduction

Nanometric dielectrics promise significant improvements of material properties for high voltage insulation. It was illustrated, that nanoparticles in polymer matrices can be used for tailored materials (1). Several publications of the past years point out the potential of using nano fillers to improve different material properties like higher electrical strength of an epoxy matrix with TiO$_2$ nanoparticles (2) or better resistance to surface degradation caused by partial discharges in polyamide and epoxy resin respectively (3–4). It is remarkable that the published improvements already occur at very low filler concentrations of 1-10 wt. %. By using conventional filler types a large amount of filler material (> 20 wt. %) is necessary to achieve the required properties (5). Yet it has not been sufficiently demonstrated, why the highest impact of nano particles can be achieved at such low filler concentrations. The present work will give an idea how to estimate the interphase fraction depending on particle diameter and interphase thickness. To evaluate the interphase thickness it is necessary to discuss the chemical and/or physical bonds in the interphase, its acting radius and the impact on material properties.

2. Interphase Structure as Crucial Parameter of Material Properties of Nanometric Dielectrics

According to recent theoretical considerations the polymer area around each filler particles is crucial for the effect of the nano particles (5–7). This area, which shall further be called interphase, should be considered as a layer with a certain thickness rather than a two dimensionial surface (10). The interphase can have a thickness of less than 1 nm (9) as well as some 10 nm (10) depending on chemical or physical bonds. In the interphase the polymer chains are chemically and/or physically bonded to the particle surface. Therefore the polymer chains can have an ordered structure, e.g. they can be arranged radially to the filler particle or in parallel to the filler surface. In either case the polymer structure differs highly from the structure of the remaining randomly arranged matrix material (Fig. 1).

The interphase structure depends on the matrix material as well as the filler type and the surface treatment where appropriate. Similar to polymers with semi crystallinity the structure of the interphase can have an influence on the properties of the polymer (15). Due to the different interphase structure and/or the bonds to the filler particle the properties of the interphase differ from the properties of the remaining matrix material.

The side chains of the polymer and the surface groups of the filler particles determine whether chemical bonds between polymer and filler exist or not. Polymer can be bonded chemically to the filler surface only if both are polar or not polar. Therefore, surface treatment of fillers and coupling agents can have a major influence...
on the interface, because nonpolar surfaces groups can become polar and vice versa.

The covalent bonds of the polymer chains have bond energies in the range of 40 - 800 kJ/mol at bond distances (atom center-atom center) between 0.075 - 3 nm \(^{(13)}\). In contrast to that the bond energies of physical bonds (mainly dipole-dipole bonds and hydrogen bonds) are in the range of 0.2 - 25 kJ/mol at bond distances of 0.5 - 0.8 nm \(^{(14)}\). Table 1 gives an overview of different bonds, their bond energies and bond distances.

The multi-core model \(^{(7)}\) proposes an interface consisting of three different layers. The first layer corresponds to a transition layer, the second layer consists of strongly bonded polymer chains and the third layer is formed by loosely coupling and interacting polymer chains. In addition, an electric double layer is overlapping the other layers \(^{(5)}\) \(^{(7)}\). This layer was not taken into account in the following estimation of interphase thickness.

The present model of the interphase is consistent with the multi-core model. In all three layers of the multi-core model the polymer chains are influenced by the filler particle and contribute to the interphase of the present model. For the estimation of the interphase fraction at different filler fractions (section 2.2) it shall be regarded sufficient to consider the different layers as one homogeneous interphase with a thickness \(i\).

The thickness \(i\) of the interphase shall be derived for the multi-core model using bond distances (Table 1) and atomic diameters (approximately 0.1 - 0.3 nm). The first layer has a thickness of approximately 1 - 1.5 nm and consists of the first tightly bonded polymer layer ha chemical bonds to the filler surface. Its thickness is the sum of the topmost layer of the particle including the bonded atom layer (approximately 0.4 nm), and the thickness of the first, tightly bonded polymer layer (approximately 0.3 - 1.0 nm) depending on polymer type.

The second layer of the multi-core model consists of the polymer chains which are physically bonded to the first (polymer-) layer or filler particle, respectively. The conformation (the steric arrangement) of the polymer chains is influenced significantly in this layer, what is the main reason for the ordered arrangement. Due to the smaller bond distance of the hydrogen-bonds and dipole-dipole-bonds this layer consists of few polymer chains in thickness if the polymer chains are arranged parallel to the filler surface. That means, the stronger the bonds, the thicker the second layer. In this case the layer can be estimated by the diameter of the polymer chains (approximately 0.3 - 1.0 nm) and the bond distances (approximately 0.5 - 0.8 nm). Two to four overlapping polymer chains with a thickness as assumed before are supposed to belong to the second layer. Therefore the layer would have a thickness of 1.5 - 8 nm. If the polymer chains are radially bonded to the filler surface, this layer can be even thicker depending on the chain length.

In the third layer of the multi-core model the polymer chains are assumed to be affected only by the position of the polymer chains of the second layer. Therefore the level of order is not as high as in the first and second layer. The thickness of this layer can vary highly and is assumed to be approximately 1 - 3 nm in thickness. Due to this consideration the resulting thickness \(i\) of the interphase can be assumed to be 3 - 12 nm.

### 2.1 Influence of the Interphase Structure on Material Properties

#### 2.1.1 Influence on the mechanical properties

Mechanical properties are highly influenced by the interphase structure. Strong physical bonds are responsible for the thickening effect caused by adding fillers. Bonds between the polymer and the filler particles can have a similar effect as a higher degree of cross-linking. Due to the higher bond energies the mechanical properties are highly influenced. For example the heat resistance, dart impact strength, the shear modulus and the tensile strength are increased \(^{(15)}\) due to the reduced flexibility of the polymer chains.

#### 2.1.2 Influence on the dielectric properties

The dielectric properties like the permittivity and the dielectric loss factor are assumed to be influenced by the mobility of the polymer chains \(^{(12)}\) \(^{(10)}\). Due to the bonds between polymer chains and filler particles and the consequently reduced mobility of the polymer chains it is presumed, that the interphase can have a permittivity other than filler and matrix material. Therefore the permittivity of the dielectric can change with large interphase fractions \(^{(10)}\).

#### 2.1.3 Influence on the electric and thermal conductivity

The electrical as well as the thermal conduction takes place along the polymer chain. Therefore, e.g. the thermal conductivity of semi crystalline polymers is higher than in amorphous polymers \(^{(15)}\). If the use of nano particles causes a higher level of order, anisotropy of the electric and thermal conductivity along the preferred direction and therefore a change in the conduction process is possible.

#### 2.1.4 Influence on resistances to material degradation

Material degradation can appear due to UV-radiation, high temperatures, corona discharges, etc. and depends on the bond energies of the polymer. Material degradation appears, if the energy is induced into the polymer and exceeds the bond energies in the polymer. In this case the bond breaks. It is mentioned.

### Table 1. Overview of different bonds, their bond energies and bond distances \(^{(14)}\)

<table>
<thead>
<tr>
<th>Bond Partner</th>
<th>Bond Distance [nm]</th>
<th>Bond Energy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C (aliphatic)</td>
<td>0.154</td>
<td>350</td>
</tr>
<tr>
<td>C-C (aromatic)</td>
<td>0.140</td>
<td>560</td>
</tr>
<tr>
<td>C=O</td>
<td>0.135</td>
<td>610</td>
</tr>
<tr>
<td>C-H</td>
<td>0.109</td>
<td>113</td>
</tr>
<tr>
<td>C-O</td>
<td>0.143</td>
<td>351</td>
</tr>
<tr>
<td>C≡O</td>
<td>0.122</td>
<td>708</td>
</tr>
<tr>
<td>C≡N</td>
<td>0.147</td>
<td>293</td>
</tr>
<tr>
<td>C-Cl</td>
<td>0.177</td>
<td>339</td>
</tr>
<tr>
<td>C-F</td>
<td>0.131</td>
<td>485</td>
</tr>
<tr>
<td>N-H</td>
<td>0.102</td>
<td>389</td>
</tr>
<tr>
<td>Si-O</td>
<td>0.164</td>
<td>444</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>0.5-0.8</td>
<td>2-12</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.5-0.8</td>
<td>3-25</td>
</tr>
<tr>
<td>dispersion forces</td>
<td>0.5-0.8</td>
<td>0.3-4</td>
</tr>
</tbody>
</table>
that due to higher bond energies e.g. C-F bonds have higher resistance to UV-radiation\(^{(14)}\) and Si-O bonds have a higher temperature resistance\(^{(15)}\) compared to C-C bonds.

Similar to this effect (due to strong chemical bonds) increased bond energies in the interphase (due to physical bonds) enhance the material resistance to degradation.

2.2 Estimation of interphase fraction at different filler fractions

The interphase fraction will be estimated by using a simplified model. The following assumptions for the filler particles are made:

1. All particles are spherical and are enclosed in an interphase of constant thickness \(i\).
2. All particles have the same diameter \(d\).
3. The particles are homogenously dispersed in the matrix material.

If the particles are dispersed homogeneously, one can define a basic element (Fig. 2), which is bordered by the centres of eight particles at each corner of the cube. The distance between the centres of neighbouring particles is \(a_0\). Furthermore it is assumed, that one particle is located in the centre of the cube having the same distance to its eight neighbours. With this particle situation a maximum filler concentration of 68 vol.\% can be achieved.

One parameter for the interphase fraction in a dielectric is the interphase thickness \(i\). Furthermore the calculation of the interphase fraction \(p_i\) is depending on the filler concentration \(V_p\). One has to differ four areas of consideration:

1. **Range of validity:** \(\frac{2}{\sqrt{3}}(d + 2i) \leq a_0\)

At low filler concentrations the filler particles have a great distance to their neighbors. The interphases of neighboring particles do not overlap (Fig. 3).

The interphase volume \(V_i\), \(V_p\) can be calculated by \(V_d + 2i\) and \(V_d\) meaning the volume of a sphere with a diameter of \((d + 2i)\) and \(d\), respectively:

\[
V_i = V_d + 2i - V_d = \frac{1}{6}\pi[(d + 2i)^3 - d^3]
\]

Comparing the interphase fraction \(p_i\) to the filler concentration \(p\):

\[
\frac{p_i}{p} = \frac{2V_i}{V_p} = \frac{(1/6)\pi[(d + 2i)^3 - d^3]}{(1/6)\pi d^3}
\]

\[
= \frac{d^3(1 + (2i/d)^3 - 1)}{d^3}
\]

That means the interphase fraction rises linearly with filler concentration.

\[
p_{i,1} = p \left[\left(1 + \frac{2i}{d}\right)^3 - 1\right]
\]

2. **Range of validity:** \(d + 2i) \leq a_0 < \frac{2}{\sqrt{3}}(d + 2i)\)

In the second area of consideration the neighboring interphases overlap. The interphase fraction is still increasing with the filler concentration but the steepness is decreasing.

\[
p_{i,II} = p \left[\left(1 + \frac{2i}{d}\right)^3 - 1\right]
- 8\left(\frac{1}{2} + \frac{i}{d} - \frac{\sqrt{3}a_0}{4d}\right)^2\left(2 + \frac{4i}{d} + \frac{\sqrt{3}a_0}{2d}\right)
\]

3. **Range of validity:** \(2\sqrt{2}/3(d + 2i) < a_0 < (d + 2i)\)

In the third area of consideration the interphases of neighboring particles highly overlap (Fig. 4). With increasing filler concentration the interphase concentration is decreasing as the filler particles occupy volume of the neighboring interphases.

\[
p_{i,III} = p \left[\left(1 + \frac{2i}{d}\right)^3 - 1\right]
- 8\left(\frac{1}{2} + \frac{i}{d} - \frac{\sqrt{3}a_0}{4d}\right)^2\left(2 + \frac{4i}{d} + \frac{\sqrt{3}a_0}{2d}\right)
- 6\left(\frac{1}{2} + \frac{i}{d} - \frac{a_0}{2d}\right)^2\left(2 + \frac{4i}{d} + \frac{a_0}{d}\right)
\]
The whole polymer consists of interphase only.

If the whole polymer consists of interphase only (Fig. 5), the interphase fraction is decreasing with increasing filler concentration.

\[ p_{i,IV} = 1 - p \]

Figure 6 shows an example of the calculation of the interphase fraction. The interphase is assumed to be 5 nm in thickness. A distinct maximum of the interphase fraction can be achieved with very small particle diameters and small filler fractions. For particles with a diameter of 10 nm a filler fraction of 10 vol.% leads to an interphase fraction of approximately 70 vol.% for example. It can be assumed, that the interphase dominates the material properties due to its high fraction. At high filler concentrations the interphase fraction is decreasing. If the filler fraction is high enough, the filler properties will have a dominant influence on the material properties. Hence, the nano effect will occur at very small particle diameters and relatively small filler concentrations. Only in this combination interphase fractions > 40 vol.% can be achieved.

(4) Range of validity: \( a_0 \leq \frac{2\sqrt{2}}{3} (d + 2i) \)

The influence of particle size at different filler fractions was investigated experimentally (11). The resistance to HV arcing was investigated according to IEC 61621. During the test procedure an HV arc is ignited on the sample surface (Fig. 8). The applied stress is strengthened by increasing the duration and the value of the current impulses every minute. The sample fails when the arc disappears while the current flows in the sample or the sample catches fire. The arcing time is defined as the duration of the test from the beginning of the test to the failure of the sample.

The investigated materials were silicone rubber filled with nano fumed silica and micro fumed silica having a mean particle diameter of 30 nm and 250 nm, respectively. With both fillers the resistance to HV arcing increases approximately linearly with increasing filler fraction and the highest resistance was achieved at the highest filler fraction of 40 wt. % (equivalent to 25 vol.%) (Fig. 9). Further, the improvement of the resistance to HV arcing with increasing filler fraction is significantly less pronounced for the material with micro filler.
In the model estimation (see Fig. 6) the interphase fraction of both materials, i.e. material with nano filler and with micro filler is increasing linearly in the investigated range of filler fraction. However, it can be noticed, that at the same filler fraction the interphase fraction by using particles having a mean diameter of 30 nm is significantly larger than by using particles with a mean diameter of 250 nm (Fig. 6). As the difference of the interphase fraction is considered to be the reason for the different arcing time, the model is in good agreement to the experimental results.

2.3 Discussion of the Model Calculation To discuss the validity of the model calculation different influencing factors are taken into consideration:

2.3.1 Particle size The particle size is one parameter in the calculation. It is assumed, that the particle diameter is constant for the whole filler material. It would be more realistic to assume a statistical distribution of the particle size. The nano particles are acting due to the interphase along the filler surface. To achieve a reasonable nano effect the particles should be separated from each other and must not agglomerate.

2.3.2 Particle shape Fillers are not ideally spherical in practice. Some fillers are rather cancelated, rod-like or layered. To assume the specific surface as the only decisive influence for the nano effect is not sufficient in either case. The appearance of filler particles can have a high influence on the properties of dielectrics. One example is given by Degussa AG: The AEROSIL ® R 8200 is hydrophobic silica very similar to AEROSIL ® R 812 S. Both fillers have a similar chemical constitution and therefore similar chemical properties and specific surfaces. AEROSIL ® R 812 S has a highly structured surface and is comparable to an unconsagted network of its primary particles comparable to usual fumed silica. Contrary to this type AEROSIL ® R 8200 has a rather compact spherical structure.

Although the materials with both silica fillers show the same mechanical properties in a RTV-2 (Room Temperature Vulcanising) silicone elastomer, the rheological properties of the material before vulcanisation differ significantly. The viscosity of the AEROSIL ® R 812 S filled material before vulcanisation is for example at 20 wt.% more than 10 times higher compared to the material with AEROSIL ® R 8200.

This example shows that the structure of filler particles can have an impact on the properties of dielectrics. Therefore the filler shape should be characterized. Furthermore it must be concluded that the models for spherical particles can not be applied for particles with other shapes in either case.

2.3.3 Dispersion of filler particles An ideal dispersion of the filler particles in the matrix material was assumed for the calculation. In this case all particles would have the same distance to their neighbors. But the distance between neighbouring particles must be regarded as being statistically distributed. Another problem is the agglomeration of filler particles. Agglomeration can be reduced by using adequate mixing methods acting with sufficient shear forces. A roller mill can be used for dispersing silica in HTV (High Temperature Vulcanizing) silicone elastomer for example. TEM (Transmission Electron Microscope) pictures can be used to evaluate the degree of dispersion.

2.3.4 Interphase thickness and structure The interphase is of significant influence on the properties of the filled material. It is difficult to calculate the exact thickness of the interphase. The thickness and the structure are influenced by the action of chemical and/or physical bonds and hence the combination of the polymer and filler, coupling agents and dispersing process. Therefore the interphase can differ in the range of few nm to several nm as discussed above.

The present model makes clear that by using nano fillers it is possible to generate materials such that most of the volume consists of interphase. For the technological impact it would be desirable of one could tailor the structure of the interphase. For example to improve resistance to degradation high bond energies in interphase are preferred.

3. Summary

(1) Based on the knowledge of the multi-core model and binding processes and the effects of particle size, thickness of the interphase and the interphase fraction have been quantified.

(2) The interphase thickness was estimated considering the bond structures in the interphase layers.

(3) The estimation of interphase fraction depending on the diameter of filler particle and interphase thickness shows a distinctive maximum of interphase fraction for filler particles with small diameters. The highest interphase fraction can be achieved for particles with very small diameters at filler concentrations of 1 - 10 vol. %.

(4) The influence of the interphase structure on mechanical properties, the dielectric loss factor, electrical and thermal conductivity as well the resistance to material degradation was discussed.
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References

(12) A. El Moussaoui, M. Kempf, and M. Scholz: “AEROSIL® Fumed Silica for Silicone Rubber- Focus on AEROSIL® R 8200 Thickening vs. Mechanical Strength”, Presentation from Technical Service AEROSIL®; Degussa AG, Hanau-Wolfgang, Germany

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