

RESISTANCE TO SURFACE EROSION OF EPOXY RESINS WITH SILICA AND ALUMINA NANOFILLERS

Johannes Seiler* and Josef Kindersberger

Laboratory for High Voltage Technology and Power Transmission,
Technische Universität München, Arcisstr. 21, 80333 Munich, Germany

*Email: <johannes.seiler@tum.de>

Abstract: The paper addresses the resistance to surface erosion of epoxy nanocomposites caused by electrical discharges depending on the type, the surface treatment and the loading of the nanofillers. For the experiments silica and alumina nanofillers are used. The spherical filler particles are produced in different ways and three different surface properties have been implemented by suitable surface treatment. Plate shaped samples with a thickness of 1 mm are tested in a rod-plane arrangement. The samples are stressed for 100 hours by surface discharges originating under normal laboratory conditions in air at the triple point when energizing the rod with a sinusoidal voltage of 10 kV at a frequency of 50 Hz. The degree of surface erosion is quantified by the eroded volume which is determined by means of a scanning profilometer. For some nanocomposites the erosion resistance increases with the filler loading up to a few percent by weight while no further increase can be observed for higher filler loadings. For other nanocomposites the resistance to surface erosion increases monotonously up to the highest filler loadings used. The observations are explained by means of the Interphase Volume Model.

1 INTRODUCTION

Polymer nanocomposites, i.e. polymers which contain few percent by weight of nanofillers (e. g. [1], [2]), can exhibit improved properties compared to conventionally used microcomposites and unfilled polymers. For example a higher resistance to surface discharges and treeing could be observed (e. g. [3]-[6]) as well as a higher resistance to high voltage arcing and to tracking and erosion (e. g. [7]). Different models were developed to explain the effect of nanofillers in polymers (e. g. [7]-[11]). They are all based on the assumption of an interfacial area, the so called interphase, between the filler particles and the polymer. In the interphase the properties can be different from the properties of the polymer and the filler particles themselves. The volume content of interphase in a composite material can be estimated by the Interphase Volume Model [7]. To study the influence of the type, the surface treatment and the loading of the nanofillers on material properties different epoxy nanocomposites were investigated by means of the resistance to surface erosion, and the thickness of the interphase around the different filler particles was estimated using the Interphase Volume Model.

2 INVESTIGATED MATERIALS

Cycloaliphatic epoxy resin and spherical silica and alumina nanoparticles were used as polymer and filler material, respectively (**Table 1**). The filler particles were produced in different ways and by suitable surface treatment. Their surface is either hydrophilic (F1, F4, F6), hydrophobic (F2, F5, F7) or epoxide groups are on the particle surface (F3).

In each case filling degrees of 1,5%, 3%, 6% and 9% were used. All types of fillers were dispersed in a planet dissolver with high shear forces using the same mixing procedure. As a reference, samples of the epoxy resin without fillers were also prepared.

Table 1: Characteristics of filler particles

filler	chemical structure	primary particle size	surface	production method
F1	SiO ₂	12 nm	hydrophilic	fumed
F2	SiO ₂	12 nm	hydrophobic	fumed
F3	SiO ₂	12 nm	epoxide groups	fumed
F4	Al ₂ O ₃	13 nm	hydrophilic	fumed
F5	Al ₂ O ₃	13 nm	hydrophobic	fumed
F6	SiO ₂	30 nm	hydrophilic	precipitated
F7	SiO ₂	30 nm	hydrophobic	precipitated

The filler dispersion was analyzed by FIB (Focused Ion Beam) images [5]. In the FIB images, particles appear as bright spots and the polymer appears black (**Figure 1**). Besides small particles some

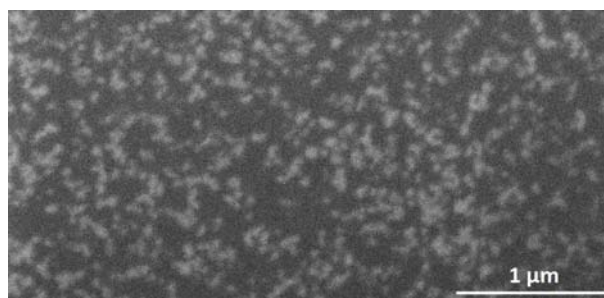


Figure 1: FIB image of an epoxy resin filled with 9 wt-% of the filler F1

agglomerates are visible. In general, the fillers can be regarded as homogeneously dispersed, whereby the degree of homogeneity increases with the filler content.

3 EVALUATION OF THE RESISTANCE TO SURFACE EROSION

3.1 Electrode arrangement and test conditions

The method to investigate the resistance to surface erosion of epoxy nanocomposites caused by electrical discharges is based on IEC 60343. The rod electrodes are made of stainless steel, they have a diameter of 6 mm and an edge radius of 1 mm (R1). In previous investigations also rod electrodes made of stainless steel with a diameter of 6 mm and a sharp edge (R0) were used [5]. In order to compare those two electrode shapes, electrodes with a sharp edge and electrodes with an edge radius of 1 mm were used for the experiments (**Figure 2**).

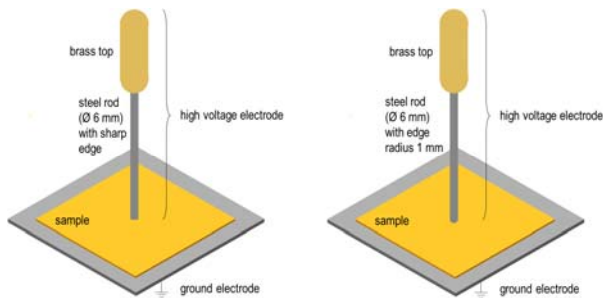


Figure 2: Electrode arrangement with electrodes with sharp edge (R0) and with an edge radius of 1 mm (R1) for the evaluation of the resistance to surface erosion of solid insulating materials

All tests described in this paper were performed at a sinusoidal voltage of 10 kV_{rms} and 50 Hz which was applied to the rods for 100 hours under normal laboratory conditions.

3.2 Evaluation of erosion

The rod electrodes are placed directly upon the sample surface and the samples are stressed by surface discharges originating at the triple point when energizing the rod with a sinusoidal voltage. After the exposure the sample surface is analysed with a laser profilometer ("Nanofocus µscan AF"). The scanning resolution used is 10 nm (x, y) and better than 0,5 µm in height (z). From the scanning data provided by the laser profilometer the eroded volume and the 95%-erosion depth are calculated within an area that is limited by an inner radius r and an outer radius R (**Figure 3**). The 95%-erosion depth is the value of erosion for which 95% of all measured points are below this value and 5% are higher than it [5].

For the following comparison of electrode shapes and evaluation methods as well as for the comparison of differently filled materials it is sufficient to discuss either the eroded volume or the 95%-erosion depth as it turned out that the tendencies that can be observed and the conclusions that can be drawn from the measurements are the same for both values.

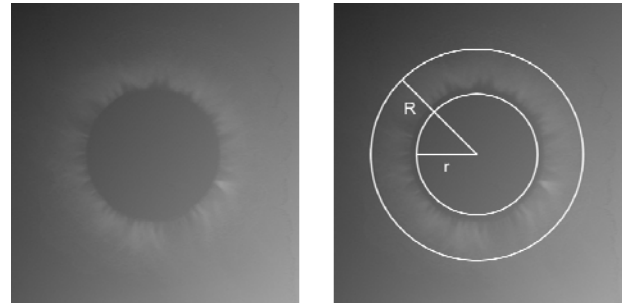


Figure 3: Surface of a sample stressed with corona discharges and inner (r) and outer (R) radius of the analysed area

3.3 Surface erosion based on direct measurements vs. measurements of silicone casts

The eroded volume is determined by scanning the sample surface which was stressed by surface discharges with a laserprofilometer. A direct scanning of the sample surface is only possible if the sample surface is not transparent, i.e. opaque. For the unfilled epoxy resin and the nanofilled epoxy resins investigated in this study this is not the case. An opportunity to determine the eroded volume of a transparent sample is to make not a direct scan of the stressed surface but to make a cast of colored RTV silicone rubber of the stressed area and to scan the surface of the silicone cast which is a negative of the stressed sample surface.

To compare the evaluation of surface erosion based on a direct measurement of the stressed sample surface with the evaluation based on the measurement of a silicone cast tests with an opaque conventional epoxy-resin with silica microfillers were conducted. Five samples with a thickness of 2 mm of this epoxy resin were exposed to surface discharges. The two electrode shapes described in **chapter 3.1** were used. After the test silicone casts with an area of 15 mm x 15 mm of the stressed surfaces were produced and the eroded volume of the stressed samples was determined by scanning the stressed surface of the samples directly and scanning the surface of the quadratic casts of the stressed sample surface with the laser profilometer. For the evaluated area an inner radius r of 2,5 mm and an outer radius R of 5,0 mm was chosen. Measurements were performed for electrodes with a sharp edge (R0) and for electrodes with an edge radius of 1 mm (R1), (**Table 2**).

Table 2: Eroded volume determined by direct measurement and by measurement of silicone casts of samples stressed with electrodes with sharp edge (R0) and electrodes with an edge radius of 1 mm (R1), 5 samples each

eroded volume [mm ³]			
direct (R0)	cast (R0)	direct (R1)	cast (R1)
0,222	0,246	0,225	0,256
0,121	0,075	0,083	0,078
0,460	0,409	0,521	0,399
0,101	0,171	0,142	0,178
0,238	0,163	0,296	0,143

To compare the direct measurement of the stressed area with the measurement of a silicone cast the empirical correlation coefficient r_{xy} was calculated (**Equation 1**).

$$r_{xy} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \cdot \sum_{i=1}^n (y_i - \bar{y})^2}} \quad (1)$$

x_i, y_i eroded volume for direct measurement and measurement of cast, respectively
 \bar{x}, \bar{y} mean value of the eroded volume for direct measurement and measurement of cast

The correlation coefficient r_{xy} for direct measurements and measurements of casts is 0,907 for electrodes with a sharp edge (R0) and 0,864 for electrodes with an edge radius of 1 mm (R1), indicating a high degree of correlation. In conclusion, the correct values for the eroded volume can be determined as well by a direct measurement of the stressed sample surface as by a measurement of a silicone cast.

3.4 Influence of the area used for the evaluation of the resistance to surface erosion

The area in which the eroded volume is determined is limited by an inner radius r and an outer radius R (**Figure 3, chapter 3.2**). Tests were conducted to compare the influence of the selection of different inner and outer radii on the eroded volume of stressed samples.

For these tests plate-shaped samples made of epoxy resin (**chapter 2**) with a thickness of 1 mm which are either unfilled or contain 1,5% to 9% of the filler F1 were stressed with surface discharges. Electrodes with a sharp edge (R0) and with an edge radius of 1 mm (R1) as described in **chapter 3.1** were used for the tests. For each filling degree the eroded volume (median and span of 5 eroded areas each) was determined for different values for the inner radius r (1,5 mm, 2,0 mm, 2,5 mm, 2,8 mm, 3,0 mm) and an outer

radius R of the evaluated area of 5,0 mm as well as for an inner radius r of 2 mm and different outer radii R (5,0 mm, 6,0 mm and 6,5 mm). As the samples investigated are transparent the evaluation of the surface erosion is based on a measurement of casts of the stressed surface areas. For easier reading the eroded volume for single filing degrees are slightly shifted from the real filling degrees (**Figure 4**).

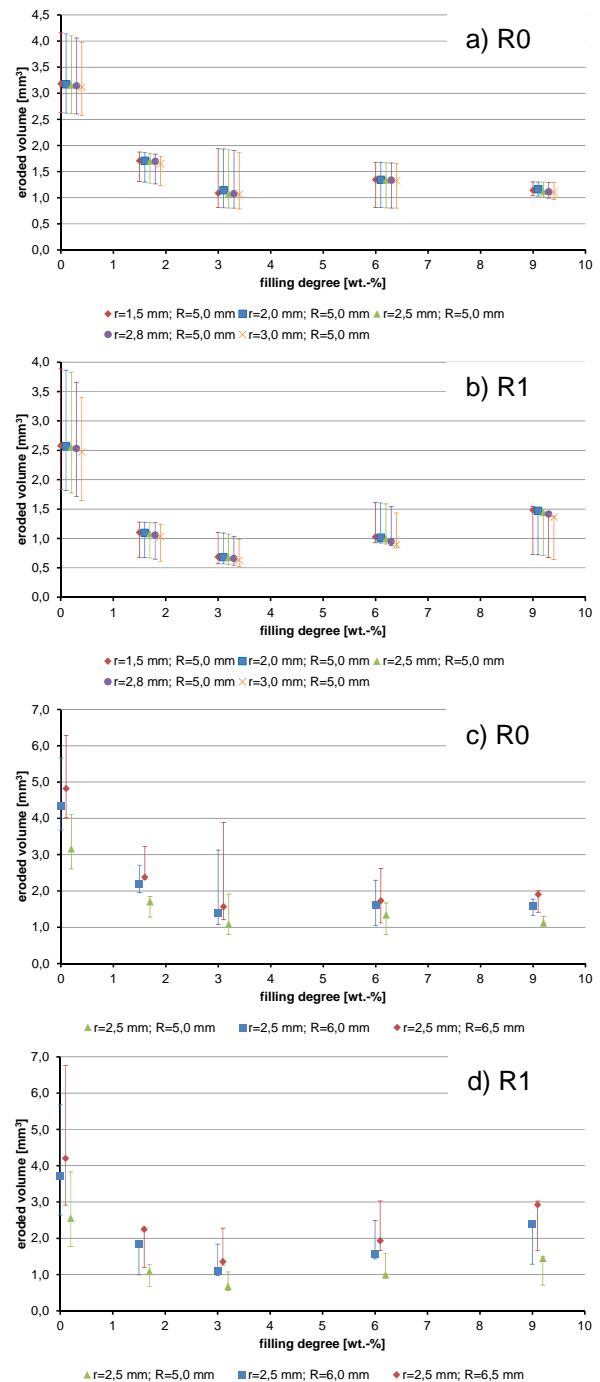


Figure 4: Eroded volume (median and span of 5 samples each) of epoxy resin samples with filler F1, stressed for 100 h at 10 kV, 50 Hz with electrodes with a sharp edge (a, c) and with an edge radius of 1 mm (b, d) for different combinations of inner (r) and outer (R) radii of the measured area

There is no significant influence of the eroded volume from the inner radius independent of the kind of the two electrode shapes used. The eroded volume is nearly the same for each filling degree for the inner radii r which were evaluated (**Figure 4 a, b**). This shows that there is no significant amount of erosion below the electrode for electrodes with sharp edges (R0) as well as for electrodes with an edge radius of 1 mm (R1). On the other hand, for both types of electrodes used an increasing eroded volume with an increasing outer radius R can be observed (**Figure 4 c, d**). With larger outer radii the span of the eroded volume becomes larger which can be attributed to asperities of the sample surface which become more dominant for larger outer radii.

3.5 Influence of electrode shape

To compare the influence of different electrode shapes on the eroded volume plate shaped samples were tested in a rod-plane arrangement. Samples with a thickness of 1 mm as described in **chapter 2** which are either unfilled or contain 1,5% to 9% of the filler F1 were used for the experiments. The rods used for the experiments have a diameter of 6 mm, they either have an edge radius of 1 mm (R1) or a sharp edge (R0) and are placed directly upon the sample surface. Five areas stressed with surface discharges were evaluated by means of the eroded volume for each filling degree and both electrode shapes. For the determination of the eroded volume an inner radius r of 2,0 mm and an outer radius R of 5,0 mm was chosen. In order to make it easier to distinguish the eroded volume for the single filling degrees the results are slightly shifted in the graphs from the real filling degree (**Figure 5**).

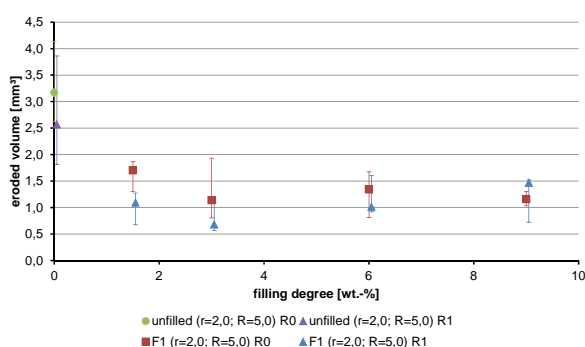


Figure 5: Eroded volume (median and span of 5 samples each) for unfilled samples and samples filled with filler F1 for an electrode arrangement with an edge radius of 1 mm and an electrode arrangement with a sharp edge

The samples stressed with rods with sharp edges (R0) show slightly higher erosion than the samples stressed with rods with an edge radius of 1 mm (R1). However, a reduction of erosion for the filled samples compared to the unfilled ones can be seen for all filling degrees. This leads to the conclusion that the influence of the filling degree

on the resistance to surface erosion is independent from the electrode shape.

4 INFLUENCE OF NANOFILLERS ON THE RESISTANCE TO SURFACE EROSION

4.1 Measurement Results

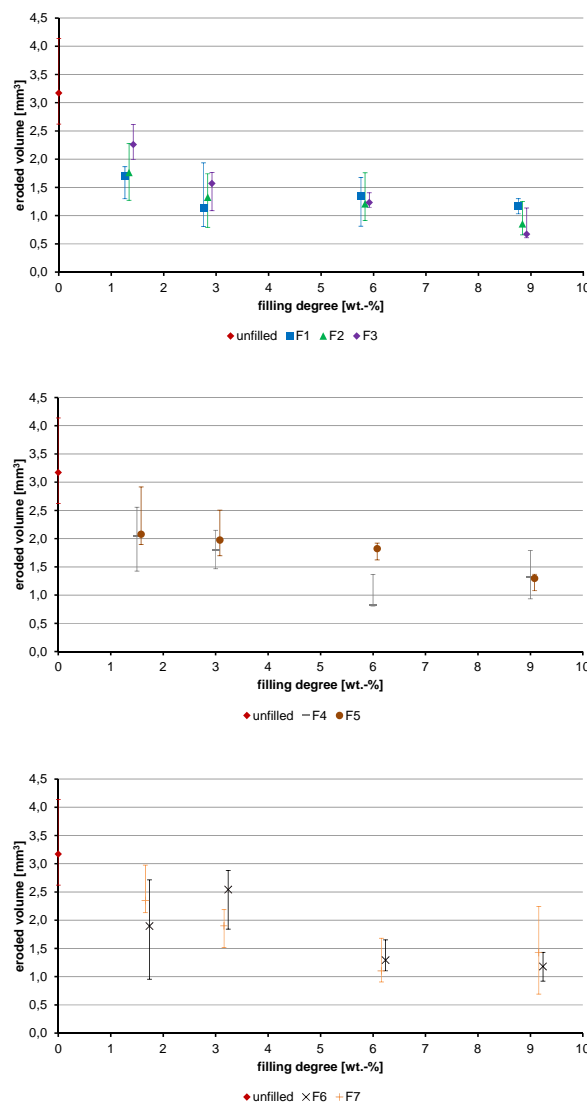


Figure 6: Eroded volume of plate-shaped samples made of epoxy resin containing different kinds of nanofillers (median and span of 5 samples each); For easier reading the eroded volume for single filling degrees are slightly displaced from the real filling degrees

Experiments on the resistance to surface erosion of epoxy nanocomposites caused by electrical discharges were conducted based on IEC 60343. Plate shaped samples with a thickness of 1 mm which contain different kinds of nanofillers (**chapter 2**) with filling degrees of 1,5%, 3%, 6% and 9% as well as the unfilled system were tested in a rod-plane arrangement. An electrode arrangement as described in **chapter 3.1** was used. The electrodes were made of stainless steel, had a diameter of 6 mm and a sharp edge. For

each filling degree the eroded volume (median and span of 5 eroded areas each) was determined for an inner radius of 2,0 mm and an outer radius of 5,0 mm of the evaluated area. The evaluation of surface erosion is based on a measurement of silicone casts of the stressed areas.

The measurement results show that type, surface property and amount of nanofillers influence the eroded volume (**Figure 6**). The median values of the eroded volume tend to decrease with increasing filler content. For epoxy resins containing the fumed SiO_2 filler F1 the lowest value of the eroded volume is achieved at a filling degree of approximately 3 wt.-%. For the epoxy resins with the fumed SiO_2 fillers F2 and F3 the eroded volume decreases monotonously up to a filler content of 9 wt.-%. For the epoxy resin containing the fumed Al_2O_3 filler F4 the highest resistance to erosion is achieved for a filling degree of approximately 6 wt.-%. For epoxy resin containing the filler F5 the resistance to surface erosion increases monotonously up to a filler content of 9 wt.-%. For epoxy with fillers of the precipitated SiO_2 types F6 and F7 a minimum of erosion is in the range approximately 6 wt.-% to 9 wt.-%.

4.2 Discussion

The volume of interphase in a composite material can be estimated using the Interphase Volume Model which assumes that all particles have the same diameters and are homogeneously dispersed [7]. The input parameters for this model are the mass densities of the matrix material ($1,2 \text{ g/cm}^3$) and the filler particles (SiO_2 : $2,2 \text{ g/cm}^3$; Al_2O_3 : $3,2 \text{ g/cm}^3$) as well as the diameters of the primary filler particles (fumed SiO_2 : 12 nm; Al_2O_3 : 13 nm, precipitated SiO_2 : 30 nm). For a defined thickness of the interphase i surrounding the filler particles a maximum of interphase volume within the composite material is achieved at different filler contents (**Figure 7**).

For example, the interphase volume content reaches its maximum for an interphase thickness of 20 nm at a filling degree of approximately 3 wt.-% of SiO_2 filler particles with a diameter of 12 nm or for an interphase thickness of 25 nm at a filling degree of approximately 3 wt.-% of Al_2O_3 filler particles with a diameter of 13 nm. For small interphase thicknesses the interphase volume content rises continuously with the filler content and no local maximum of interphase volume appears for filling degrees lower than 9 wt.-%.

It is assumed that the highest improvement of the resistance to surface discharges is achieved with the highest content of interphase volume within the composite material. As a consequence, the highest resistance to surface erosion of differently filled epoxy resins (**Figure 6**) should be achieved near the maximal interphase content (**Figure 7**).

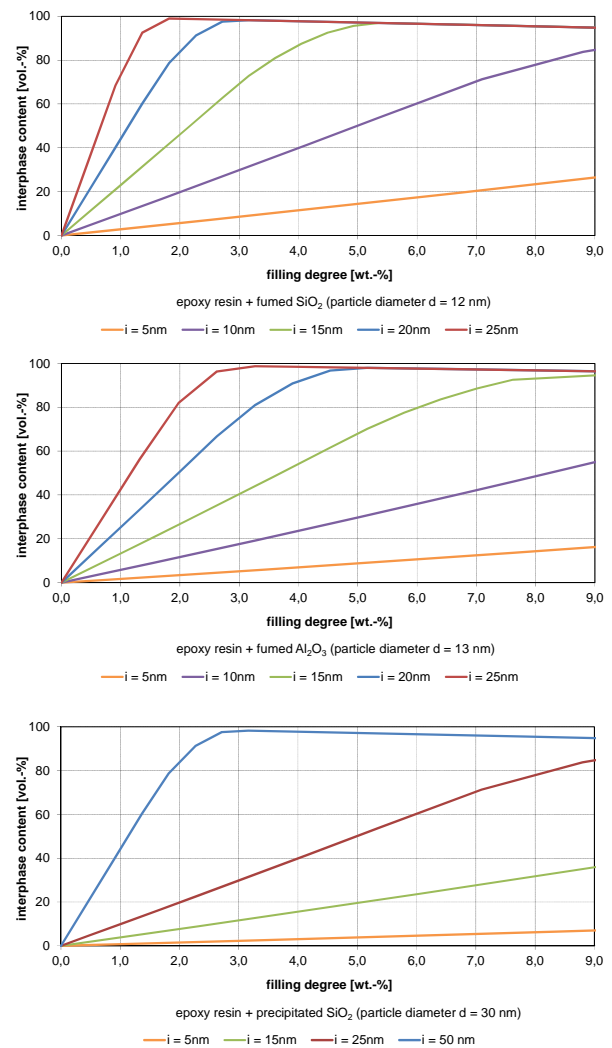


Figure 7: Portion of interphase in a nanocomposite depending on the interphase thickness, the filler particles and the matrix material used (epoxy resin), the particle diameter and the filling degree, according to the Interphase Volume Model

For the materials investigated in this study the unfilled system shows the highest eroded volume.

For the fumed SiO_2 filler F1 a local minimum of erosion is achieved for a filling degree of approximately 3 wt.-%. For a filling degree of 3 wt.-% of fumed SiO_2 particles with a diameter of 12 nm the interphase volume content reaches a local maximum for an interphase thickness of approximately 20 nm. For filling degrees higher than 3 wt.-% of the fillers F1 the resistance to surface erosion remains almost constant as the interphase volume content does for an interphase thickness of 20 nm around fumed SiO_2 filler particles. For epoxy resin with the fillers F2 and F3 the eroded volume is decreasing monotonously up to a filling degree of 9 wt.-%. This can be explained by an interphase volume content that is monotonously increasing with the filling degree and does not reach a local maximum for filling degrees below 9 wt.-%. This is the case for an interphase

thickness of 10 nm or even lower around fumed SiO₂ nanoparticles with a particle diameter of 12 nm.

For epoxy resin with the fumed Al₂O₃ filler F4 the minimum of erosion appears at a filling degree of 6 wt.-% corresponding to an interphase thickness between approximately 15 nm and 20 nm. A monotonously decreasing surface erosion can be observed for epoxy resin filled with the filler F5 which can be explained by an interphase thickness of 10 nm or lower around the fumed Al₂O₃ nanoparticles.

For epoxy resin with the fillers F6 and F7 a minimum of erosion is achieved for filling degrees in the range of 6 wt.-% to 9 wt.-%. This can be explained by a thickness of the interphase of approximately 15 nm around precipitated SiO₂ nanoparticles with a diameter of 30 nm.

In summary the measurement results for the resistance to surface erosion can be explained by different interphase thicknesses around the filler particles and are in good agreement with the estimated interphase volume content. There seems to be an influence of the type of filler, the manufacturing process of the filler and the surface properties of the filler on the thickness of an interphase existing around the filler particles.

5 CONCLUSION

The resistance to surface erosion of epoxy resins with different silica and alumina nanofillers was investigated with a rod-plane arrangement based on IEC 60343.

The following results were achieved:

- The influence of the filler content on the resistance to surface erosion is independent of the electrode shape (sharp edge or edge radius of 1 mm) and the area used for the evaluation.
- The resistance to surface erosion is significantly influenced by the filling degree. Depending on the type of filler and the surface treatment the resistance to surface erosion either shows a local maximum or increases monotonously with the filler content.
- The influence of the filling degree on the resistance to surface erosion can be explained by the Interphase Volume Model.

6 ACKNOWLEDGMENT

The authors want to thank Dr. M. Scholz, U. Schachtely and C. Schlegelmilch (EVONIK Industries) for providing fillers and preparing samples, Dr. H. Wilbers (HUNTSMAN) for providing epoxy resin as well as Prof. Dr. D. Schmitt-Landsiedel and Dr. M. Becherer for granting access to and for operating the FIB (Institute for Technical Electronics, TU Muenchen).

7 REFERENCES

- [1] Nelson, J.K.: Dielectric Polymer Nanocomposites; Springer New York; 2010
- [2] CIGRE WG D1.24: Polymer Nanocomposites - Fundamentals and possible applications to Power Sectors; Technical Brochure No 451; 2011
- [3] Rätzke, S.; Ohki, Y.; Imai, T.; Tanaka, T.; Kindersberger, J.: Tree Initiation Characteristics of Epoxy Resin and Epoxy/Clay Nanocomposite; IEEE TDEI, Vol. 16, No. 5; pp. 1473 – 1480; 2009
- [4] Weidner, J.R.; Pohlmann, F.; Gröppel, P.; Hildinger, T.: Nanotechnology in High Voltage Insulation Systems for Turbine Generators – First Results; Proc. XVII. ISH; Hannover, Germany; August 22-26; 2011
- [5] Anglhuber, M.; Kindersberger, J.: Quantification of Surface Erosion and Microscopic Analysis of Particle Distribution in Polymer Nanocomposites; IEEE TDEI, Vol. 19, No. 2; April 2012
- [6] Krivda, A.; Kindersberger, J.; Tanaka, T.; et al.: Characterization of Epoxy Microcomposite and Nanocomposite Materials for Power Engineering Applications; IEEE Electrical Insulation Magazine; Vol., 28, No. 2, pp. 38-51; 2012
- [7] Raetzke, S.; Kindersberger, J.: Role of Interphase on the Resistance to High-voltage Arcing, on Tracking and Erosion of Silicone/SiO₂ Nanocomposites; IEEE TDEI, Vol. 17, Issue 2, pp. 607-614, 2010
- [8] Lewis, T.J.: Interfaces are the Dominant Feature of Dielectrics at the Nanometric Level; IEEE TDEI; Vol. 11, No. 5, pp. 739-753; 2004
- [9] Tanaka, T.; Kozako, M.; Fuse, N.; Ohki, Y.: Proposal of Multi-core Model for Polymer Nanocomposite Dielectrics; IEEE TDEI; Vol. 12, No. 4, pp. 669-681; 2005
- [10] Andritsch, T.: Epoxy Based Nanocomposites for High Voltage DC Applications – Synthesis, Dielectric Properties and Space Charge Dynamics; Dissertation TU Delft; 2010
- [11] Tanaka, T.; Imai, T.: Advances in Nanodielectric Materials Over the Past 50 Years; IEEE Electrical Insulation Magazine; Vol. 29, No.1, pp.10-23; 2013