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Increasing the electrical discharge endurance of acid anhydride cured DGEBA epoxy resin by dispersion of nanoparticle silica

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Abstract. A fluid DGEBA/methyl nadicanhydride epoxy system has been filled with inorganic particles, cast as bubble-free plates and cured. The ability of both the pure network polymer and the polymer/particle composites to withstand partial electrical discharges has been investigated. Three types of particle combinations were used: (a) fumed nanoparticle silicon dioxide referred to as Aerosil, (b) equal volumes of Aerosil and nanoparticle anatase, and (c) Aerosil plus anatase in combination with coarse-particle filler grade calcium–magnesium carbonate dolomite. A test for endurance using the CIGRE method II electrode arrangement was applied, the test comprising the establishment of partial discharges running perpendicularly onto one face of a plate specimen for a period measured until breakdown.

Our results show that the endurance of the pure polymer is low. Increased loading with Aerosil increases the endurance by a factor of up to 20 as the Aerosil content goes from zero to 5.4 vol.%. Aerosil mixed with anatase has a similar effect. The high level of endurance is maintained with an additional high-volume (35 vol.%) filling of coarse-particle dolomite to an epoxy system already containing Aerosil and anatase. The results are discussed in the light of estimated interparticle spacings and interface areas.

1. Introduction

The present paper is concerned with an acid anhydride cured DGEBA epoxy resin having a small content of amorphous silica nanoparticles, up to 5 vol.%. It is our intention to present results showing that nanoparticle silicon dioxide Aerosil, when well dispersed in the polymer, has the effect of substantially increasing the endurance of the polymer when exposed to partial electrical discharge (PD) by a specific test. Moreover, we show that Aerosil has a similar effect on epoxy plastic filled with an ordinary coarse-particle mineral filler, dolomite, although it is known from the literature that dolomite filling of epoxy plastic alone has the reverse effect of decreasing the PD endurance.

We use the word nanoparticle when the particle size is so small that it must be measured in nanometres rather than micrometres. This is in order to distinguish nanoparticles from ordinary coarse-particle fillers of micrometre particle size.

It is well known that the surface of polymeric insulation is damaged by the occurrence of a PD. Permanent damage showing signs of polymer evaporation, erosion, melting, charring and fracture may all appear and may lead to electrical breakdown and thus the end of the life

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of a polymer-insulated electrical component. Polymer surfaces exposed to a PD may be free outer surfaces as well as surfaces having internal voids and cavities in a polymer body. The said voids and cavities may be present as an unintentional factor in commercial insulation.

The specific test used by the present authors is due to Kako *et al* [1]. It has become known as the CIGRE method II. In this test the PD is established as electric gas discharges in a narrow gap between a plane metal electrode and the plane surface of the polymer covering an opposing metal electrode. The polymer is invariably present as a 1 mm thick plate. The endurance is measured as the length of time in hours until breakdown in the polymer, i.e. the formation of a hole in the specimen.

1.1. Fillers in epoxy systems

It is a well established technique to add coarse-particle mineral fillers when casting epoxy plastics for use in constructing electrical insulation components. Fillers have the effect of reducing shrinkage during cure, thereby reducing internal stress and strain. Moreover, fillers also increase the thermal conductivity and reduce the thermal expansion coefficient. The combined effect is evident in the reduced tendency of a filled system to fracture during service with a reduced risk of the occurrence of a damaging PD in the fracture cracks and thereby a prolonged service life of the component.

In a comparative study of filled epoxy systems [2] it has been observed that fillers with ordinary particle sizes above 1 μm and up to 40 μm in loadings of 32–41 vol.% have the effect of reducing the endurance as shown by the PD test when compared with the pure epoxy system. The fillers used were alumina Al_2O_3, dolomite $CaCO_3$, $MgCO_3$ and silica quartz SiO_2. This finding is in accord with other observations using the same method [3] on a silica filled system. It has also been observed by an alternative method [4].

The epoxies in [3] and [4] are exclusively Araldite products of CIBA-Geigy. Their chemical compositions have not been published. While the epoxy resins are believed to be DGEBA, the curing agents are unknown. In [2] Epikote 828 from Shell is also included, this is a well defined DGEBA cured with methyl nadic anhydride MNA and accelerated by benzyl dimethylamine BDMA.

1.2. Previous studies on nanoparticles in epoxy systems

It has been observed previously [2] that anatase TiO_2 having a particle size below 400 nm has the effect of increasing the endurance of epoxies as shown by the PD test when applied in 5 vol.% loading. An even larger effect is shown by Aerosil SiO_2 having a particle size below 10 nm when applied in 5.4 vol.% loading [2, 5].

It has also been observed [2, 6] that 5 vol.% anatase has the effect of preventing the settling of coarse fillers in fluid epoxy systems. Thereby a uniform distribution of coarse fillers in cast epoxy plastic plates is obtained. Aerosil is not found to have this anti-settling effect at the elevated temperatures necessary for curing of the present epoxy system, but it impedes the settling of coarse particles.

1.3. Materials investigated in the present work

The epoxy system in use here is fluid DGEBA epoxy resin Epikote 828 cured with methyl nadic anhydride MNA and accelerated by benzyl dimethylamine BDMA. When the particle size of fillers is well below 1 μm it becomes difficult to disperse a large volumetric amount in fluid epoxy systems because of increased viscosity and the onset of some thixotropy. Moreover, processing steps such as degassing in a vacuum and casting become increasingly difficult the higher the amount of filler. Five per cent on a volume basis is found by the present authors to be near the maximum loading.

The effect of Aerosil on endurance found by the PD test is studied in the range from 0 to 5 vol.% loading in the epoxy system. Moreover, the combined effect of equal parts of Aerosil and anatase is investigated by the PD test on both the plain epoxy system and the same epoxy system when filled with coarse-particle dolomite filler.

2. Experiment

The experimental details of the present work comprise three steps: (a) polymer plate specimen preparation, (b) electrode preparation and specimen mounting and (c) the PD test. This section briefly describes the experiment, while an extended version is presented in the appendix.

The essential features of the specimen and the electrode system are shown in figure 1. This assemblage, held by a clamping device, is immersed in oil during the test.

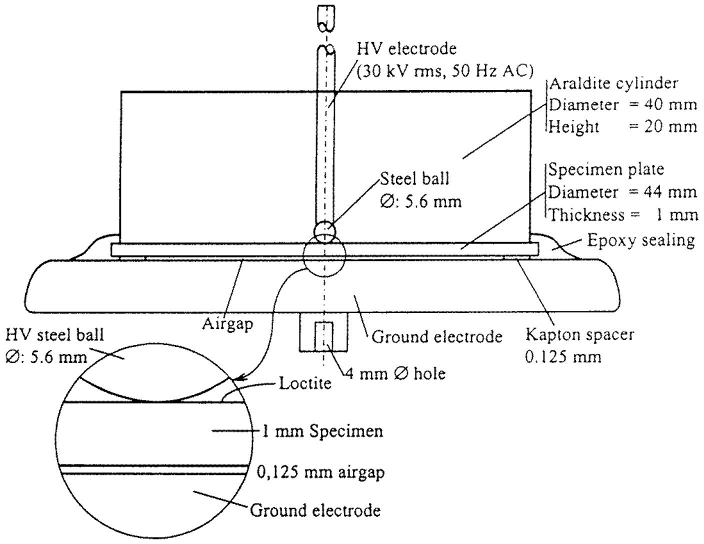

Figure 1. The specimen and air gap mounted between ball and plate electrodes.

2.1. Polymer plate specimen preparation by casting

Ingredients: DGEBA epoxy resin Epikote 828 (Shell); MNA methyl nadic anhydride (Taab laboratories equipment); BDMA *N*-benzyl dimethylamine (Fluka, purum); Aerosil fumed silica (Degussa); anatase titanium dioxide (E Merck, lab grade) and dolomite calcium magnesium carbonate (unknown origin, filler grade).

Densities: pure epoxy polymer after cure 1220 kg m^{-3} by buoyancy in water; aerosil 2140 kg m^{-3} calculated from the density of epoxy/Aerosil composite; anatase 3900 kg m^{-3} by pyknometry; dolomite 2860 kg m^{-3} by pyknometry.

Particle sizes: Aerosil around 7 nm [7]; anatase weight average 240 nm, 10% $>$ 330 nm from sedimentation in sedigraph; dolomite weight average 21 μm, 10% $>$ 43 μm, 10% $<$ 6 μm from sedimentation in sedigraph.

Table 1. Masses in g for 100 cm^3 of composite.

Aerosil (vol.%)	0	1	2	3	4	4.73	5	2.36	2.36
Anatase (vol.%)								2.36	2.36
Epoxy (vol.%)	100	99	98	97	96	95.27	95	95.28	95.28
Epoxy phase (vol.%)	100	100	100	100	100	100	100	100	65
Dolomite (vol.%)	0	0	0	0	0	0	0	0	35
DGEBA	65.52	64.86	64.21	63.55	62.90	62.42	62.24	62.43	40.58
MNA	55.04	54.49	53.94	53.39	52.84	52.44	52.29	52.44	34.09
BDMA	1.44	1.43	1.41	1.40	1.38	1.37	1.37	1.37	0.89
Aerosil		2.14	4.28	6.42	8.56	10.12	10.70	5.05	3.28
Anatase								9.20	5.98
Dolomite									100.10
Number of plates	5	1	1	1	1	5	1	2	2

Mass ratio for the epoxy system: DGEBA/MNA/BDMA = 100/84/2.2. The curing schedule for all preparations was 80 °C for not less than 8 h, immediately followed by 150 °C for 15 h.

It is essential for a successful PD test that the plates are free of bubbles. This is achieved by the extensive use of degassing, here exclusively evacuation in a vacuum desiccator or chamber until all bubbles have disappeared, i.e. vacuum down to 0.02–0.01 Torr = 260–130 Pa.

In all, nine different compositions were made into plate specimens. Table 1 shows the mass ratios of the ingredients for each composition. Nanoparticles dispersed in the polymer are in the table included in the epoxyphase.

Plate casting: for one plate, ingredients corresponding to 4–6 cm^3 of composite are mixed in an order corresponding with the vertical listing of table 1. Each step is followed by degassing. A quantity of the mixture corresponding to 2.5 cm^3 is cast between two Balinit A coated steel plates (Balzers Sandvik Coating) in a horizontal position. These steel plates were kept 1 mm apart by three spacers. The resin is cured in an oven, cooled to about 50 °C, the plastic plate is released from the steel, cut to a 44 mm diameter roundel and ground on the edge with carborundum paper.

2.2. *Electrode preparation and specimen mounting (see figure 1)*

There are two electrodes, one high voltage, HV, and one ground, GR. The HV electrode is embedded in an insulating block cast in Araldite. The specimen is fastened to the HV by Loctite cyanoacrylate adhesive. Between the specimen and GR there is a 0.125 mm air gap, the distance given by a Kapton spacer. The joint (specimen plate/spacer/GR) is sealed by a room-temperature curing Epofix (Struers). All parts are ultrasonically rinsed in ethanol before mounting. Sealing is performed with the parts held in a clamping device which remains with the specimen during the test.

2.3. *PD test*

During testing the whole assemblage (specimen/electrodes/clamping device) is immersed in silicone oil, only part of the HV brass rod being above the oil level. Five specimens can be tested simultaneously at 30 kV rms 50 Hz a.c. fed from a 1% stabilized 220 V power mains.

Table 2. Endurance of epoxy plastics by the PD test.

Aerosil (vol.%)	0	1	2	3	4	4.73	5	2.36	2.36
Anatase (vol.%)								2.36	2.36
Epoxy (vol.%)	100	99	98	97	96	95.27	95	95.28	95.28
Epoxy phase (vol.%)	100	100	100	100	100	100	100	100	65
Dolomite (vol.%)	0	0	0	0	0	0	0	0	35
Endurance	55					306			
(h)	111	108	312	548	517	1050	1248	263	420
	113					>1050†		1725	1813
	114					1190			
						1289			

† After 1050 h of PD this test was terminated before breakdown occurred. The assemblage was opened and the specimen was examined by microscopy.

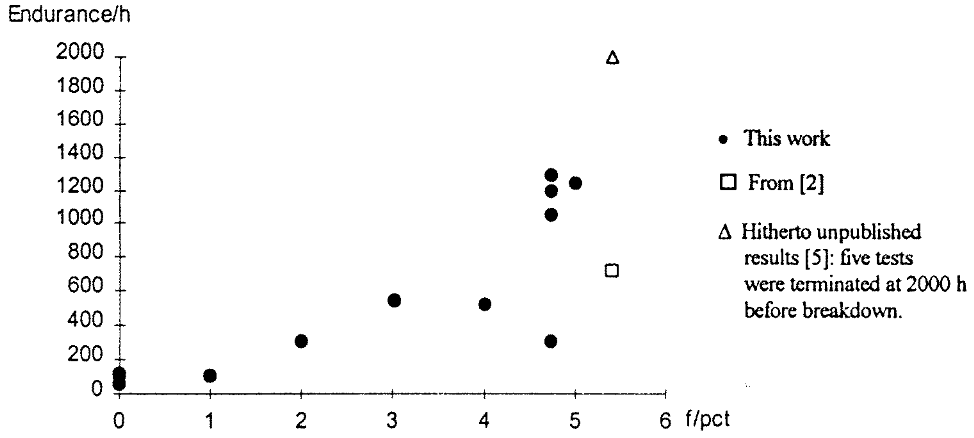

Figure 2. The increase of PD endurance as the Aerosil content f in epoxy plastic is increased.

The connection to the HV electrode of each of the five specimens carries a 50 mA fuselink which operates when the corresponding specimen breaks down. An operated fuse is visible at a suitable distance and thus marks the end of the endurance of the corresponding specimen.

Regular inspection of the test set-up three times per 24 h and three times during week-ends gives a deviation on the observed endurances of 8 to 20 h.

3. Results

The results comprise two sections: endurance and appearance of damaged polymer.

3.1. Endurance

The endurance in hours of each specimen is listed in table 2. For the specimens containing Aerosil only, the endurances are also displayed on the graph in figure 2 showing increasing endurance as the Aerosil content increases from zero to the level of about 5 vol.%, beyond which the viscosity of the uncured material becomes prohibitively high for degassing and casting.

Table 3. Endurance of pure and filled DGEBA based systems cured with acid anhydrides. GIGRE method II, room temperature, 30 kV rms, 50 Hz.

						Endurance (h)			
Epoxy	Epoxy phase, additive		Filler, coarse particle	No. of specimens	Remark	Lowest	Median	Highest	Ref.
a	Pure epoxy			9	Note a	0	58	104	2
			Dolomite 39 vol.%	5		2	10	21	2
			Alumina 32 vol.%	10		10	60	88	2
			Silica 41 vol.%†	5		5	26	>262	2
b	Pure epoxy			10	Note b	130	210	300	1
	Has flexibilizer	4.5 wt%		10		170	220	310	1
				7		260	280	400	1
				149	Note 1	2	150	664	3
				130	Note 2	42	150	240	3
				5		156	180	254	8
			Silica 49 vol.%‡	43	Note 3	30	100	270	3
		9 wt%		4		113	125	158	8
c	Pure epoxy			8	Note c	55	100	214	2
				4	Note c	55	112	114	t.w.
	Has nanoparticles	Anatase 5 vol.%		5		3	426	>528	2
		Anatase 5 vol.%	Dolomite 35 vol.%	5		145	407	>645	2
		Aerosil 1 vol.%		1			108		t.w.
		Aerosil 2 vol.%		1			312		t.w.
		Aerosil 3 vol.%		1			548		t.w.
		Aerosil 4 vol.%		1			517		t.w.
		Aerosil 4.73 vol.%		5		306	1150	1289	t.w.
		Aerosil 5 vol.%		1			1248		t.w.
		Aerosil 5.4 vol.%		1			725		2
		Aerosil 5.4 vol.%		5			>2000		5
		Anatase 2.36 vol.% +Aerosil 2.36 vol.%		2		263		1725	t.w.
		Anatase 2.36 vol.% +Aerosil 2.36 vol.%	Dolomite 35 vol.%	2		420		1813	t.w.

Table 3. (Continued)

Particle sizes	10% <	w.average	10% >
Dolomite	6.0 μm	21 μm	42.5 μm
Alumina	5.1 μm	8 μm	11.7 μm
†Silica	1.0 μm	5 μm	14.1 μm
‡Silica		No information	
Anatase		240 nm	330 nm
Aerosil		7 nm	

In the reference column t.w. refers to this work while the numbers refer to the reference list.

a: Araldite CY 225(100) + HY 925(80). (The numbers in brackets are mass proportions.)

b: Araldite CY 205(100) + HY 905(100) + DY 061(1). Flexibilizer = DY 040.

c: Epikote 828 (100) + MNA (84) + BDMA (2.2).

1: All data.

2: 10% extreme data reduction, 130 out of 149 from note 1.

3: 10% extreme data reduction, 43 out of 52. The volumetric filling of 49% has been calculated by us. Reference [3] states 400 parts of silica to 200 parts of epoxy resin + curing agent by weight. No information about particle size.

Comparison:

System **a** has the lowest endurance compared with **b** and **c** when free of fillers and additives. Coarse-particle filling tends to reduce the endurance except when filling with alumina. Dolomite filling gives a strong reduction.

System **b** has the highest endurance when free of fillers and additives. The use of a moderate amount of flexibilizer (4.5%) may reduce the endurance. A larger amount (9%) reduces the endurance. A coarse-particle silica filling reduces the endurance.

System **c** is the system used in the present work. When free of fillers and additives it has a medium endurance. Nanoparticle filling with anatase increases the endurance to high levels. An even stronger effect is shown by nanoparticle Aerosil filling. An additional filling with coarse-particle dolomite maintains the high level of endurance.

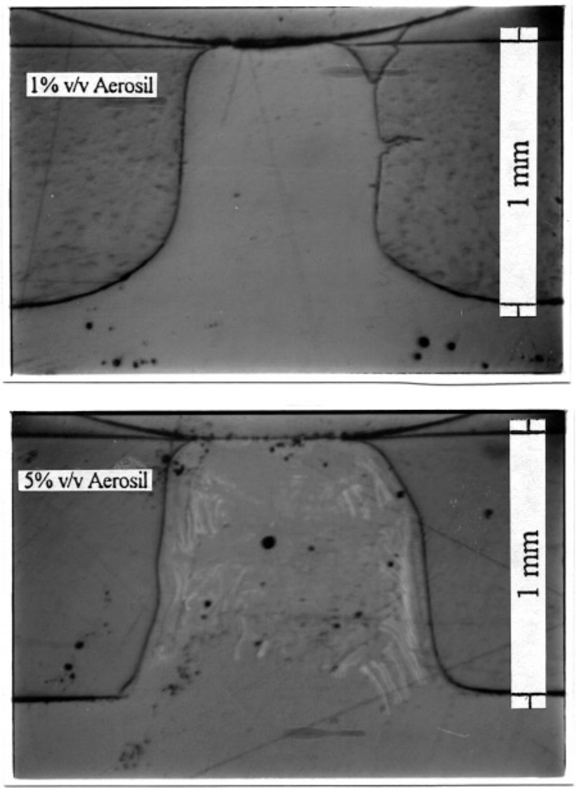

Figure 3. Micrographs of breakdown holes in epoxy plastics after PD test. Axial cut. Top, 1 vol.% Aerosil; bottom, 5 vol.% Aerosil. Reflected light. The HV steel ball has been etched away for proper flatness in grinding. Fractures are visible on the top specimen.

3.2. Appearance of damaged polymer

By inspection of all the specimens after the test it was observed that a breakdown manifests itself as an axial hole through the plate right under the steel ball. The diameter of the hole is larger on the cavity side where erosion starts than on the steel ball side. This is shown in the micrographs of figure 3.

Moreover, concentric with the hole there is a circular area—visible to the naked eye and approximately 10 mm in diameter—where the cavity surface is matt. This area is not sharply delimited, the matting fading outwards. Both the ground electrode and the specimen carry a black deposit of erosion products, presumably charred material.

Cleaning with acetone and wiping off the deposit reveal the surface to be pitted on the matt area while outside it is blank and mirror like. The pitting is illustrated in figure 4 by micrographs of an axial cut in the specimen having 1050 h of PD, the test being terminated before breakdown occurred.

4. Discussion

It may be useful in table 3 to compare the present results on nanoparticle filled epoxy with published results on pure epoxy and coarse-particle filled systems although these are not always well defined with respect to the epoxy system and in one case with respect to the filler used.

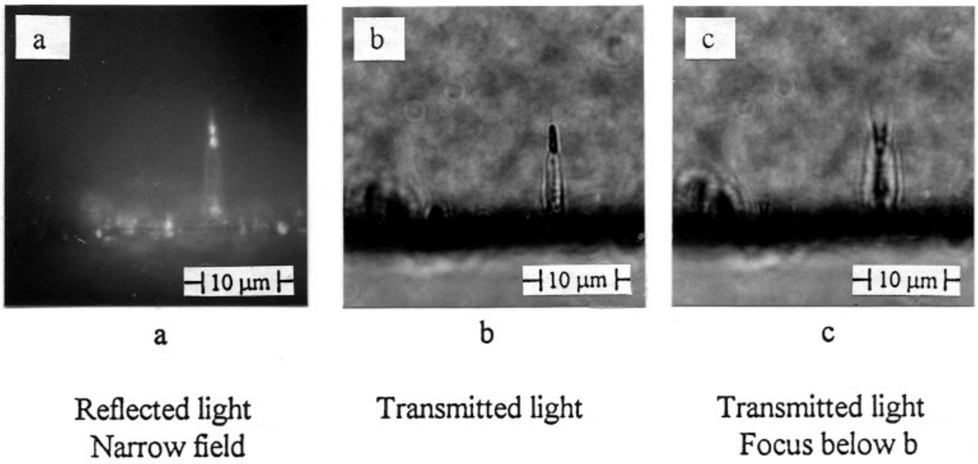

Figure 4. Micrographs showing erosion pits on the face of a specimen facing the cavity of a PD assemblage. The specimen contains 4.73 vol.% Aerosil. 1050 h of PD, no breakdown. Axial cut, centrally under HV electrode, ground and polished to a thickness less than 0.1 mm. The black V formation in the bottom of the large pit on (*c*) could suggest the beginning of an electric tree growth.

It is not likely that the beneficial effect observed on PD performance by the presence of nanoparticles in both plain and dolomite filled epoxy can be understood by purely electrical bulk properties of the particle materials. In the case of Aerosil it is amorphous SiO_2 of low permittivity ($\varepsilon_r = 3.8$) and high resistivity, while in the case of anatase it is crystalline TiO_2 of high permittivity ($\varepsilon_r = 48$) and low resistivity. This compares with a permittivity of 3.7 in the pure epoxy system.

4.1. The effect of partial discharges on a polymer

Partial discharges are repetitive, i.e. within each period of the a.c. supply voltage there will be a number of discharge pulses each of short duration, about 10^{-7} s [9]. The observations of the matt part of the surface area and the hole of the broken-down specimens indicate that the PD most frequently will impinge on the specimen vertically under the HV ball electrode.

Each discharge—being the consequence of an avalanche mechanism bridging the gap—is a momentary high-energy plasma channel, the plasma containing electrons of high concentration in front of an avalanche growing in a direction towards the positive terminal, and positive ions (N_2^+, O_2^+, N^+ and O^+) in the tail moving slowly towards the negative terminal. Moreover there are excited molecules emitting photons to the gap and the surrounding materials including the specimen.

It is far from clear how this energy is being dissipated by the insulating epoxy system. The following is an attempt to explain the results in a qualitative way.

A momentary pulse-like heating concentrated on a polymer surface layer at the foot point of a discharge will be the result of at least three actions, namely the bombardment by ions and electrons, the current density in the polymer at the foot point, and the absorption of photon energy. A mechanical impact will be the result of at least two actions, namely the bombardment by ions and the effect of the high concentration of electrons in the front of an avalanche growing in direction towards the polymer: as the front approaches the polymer a pull will be exerted on the atomic nuclei and a push on the electrons, the forces being stronger the shorter the distance.

Localized excessive heating of the polymer will lead to bond scission, i.e. thermal degradation and the formation of small molecules. Localized mechanical impact will lead to bond scission and erosion. Moreover, oxidation of the polymer will take place. All in all these conditions do not favour long-term stability of the epoxy or any other organic polymer.

4.2. The effect of PD on filled epoxy

The damage due to a PD on filled epoxy may be delayed if the filler particles have the possibility of exerting an effect of being thermal shields or heat sinks.

In general, inorganic fillers are stable at higher temperatures than polymers: dolomite is degraded by the evolution of carbon dioxide above 650 °C, anatase shrinks by transforming into denser rutile at about 700 °C, rutile itself melting at 1640 °C, and amorphous silica has a glass transition temperature of 1100 °C while the epoxy starts thermal degradation at about 300 °C. On this basis a shield effect might be expected.

While the specific heat per unit volume of the filler materials and the epoxy are comparable in magnitude (in MJ m^{-3} the values are dolomite 2.5, anatase 2.8, amorphous silica 1.6, epoxy 2.5 all at room temperature, all increasing with temperature) the thermal conductivity of the inorganic filler materials is higher than the thermal conductivity of epoxy by a factor of more than 5 (in W m^{-1} K^{-1} the values are dolomite 1.1, anatase unknown (rutile 8.4), amorphous silica 1.4 against epoxy 0.2). On this basis a heat sink capacity might be expected for thermal pulses.

The observations from [2] on epoxy **a** in table 3 indicate that the coarse particles of dolomite, alumina and silica in high fractions of filling have neither a shield effect nor a heat sink effect.

On the other hand, the results from the present work and [2] on epoxy **c** in table 3 indicate that a key to an explanation for the effect of nanoparticle Aerosil and anatase in relatively small fractions of filling may be found in two textural properties accompanying particle filling in polymers, here related to a decrease in particle size:

(a) The interparticle spacing decreases, this is often overlooked as pointed out by Rohan and Hancock [10].
(b) The polymer/particle interface area increases.

4.3. Ball model, interparticle spacing, and interface area

A simple ball model of a particle-filled polymer illustrates the order of magnitude for both interparticle spacing and interface area. Consider the—unlikely—situation of ball particles all having the same diameter D and being uniformly distributed, thus neglecting aggregates and agglomorates of particles. Moreover, assume that each ball has six nearest neighbours at a volumetric filler loading fraction f. This ball equivalent model will be characterized by

$$\text{nearest neighbour spacing} = D[(\pi/6f)^{1/3} - 1]$$

$$\text{polymer/particle interface area per volume unit} = 6f/D.$$

A calculation for ball particle loading with $D = 7$ nm corresponding to Aerosil and f in the range from 0.01 to 0.05 (1 to 5 vol.%) gives spacing decreasing from 20 to 8 nm while the area increases from 9 to 40 km^2 m^{-3} as illustrated in figure 5.

Corresponding to anatase, calculation for $D = 240$ nm and $f = 0.0236$ gives a spacing of 597 nm and an area of 0.59 km^2 m^{-3}. For dolomite $D = 20\,000$ nm, $f = 0.35$, calculation gives a spacing of 2900 nm and area of 0.1 km^2 m^{-3}, i.e. a considerably wider spacing and smaller area.

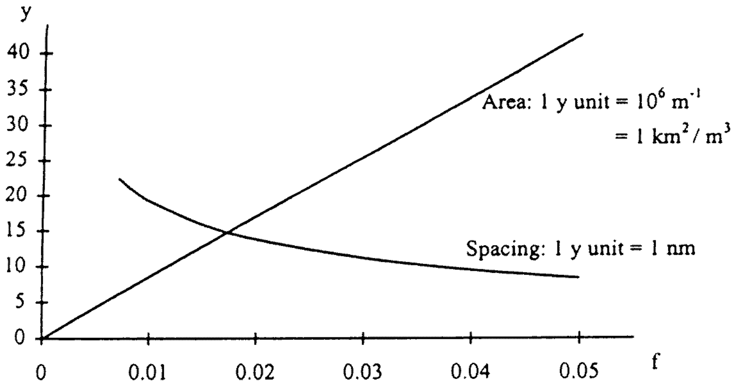

Figure 5. Spacing and area depending on f at $D = 7$ nm for a ball equivalent model.

4.4. The influence of coarse particles and nanoparticles on PD

The typical effect of particle size and volumetric loading is that with coarse-particle fillers in high loading the interparticle spacing is in the micrometre range while nanoparticles in low loading give interparticle spacing in the nanometre range. A consequence of this difference may be that with coarse particles the discharges by thermal degradation and erosion will damage a thick epoxy layer before they reach a coarse particle and then will work their way around it because there is a large epoxy spacing to a neighbouring particle, i.e. there is hardly any shield or heat sink effect. With nanoparticles the surface layer is much thinner so that a delay is introduced by the particles acting as a distributed heat sink and thereby shielding the epoxy behind and in the narrow spacings between the particles. The higher the loading with nanoparticles the larger will be the volume temporarily absorbing the thermal energy of a discharge, and the larger will be the interface area through which the thermal energy has to pass.

5. Conclusion

The major achievement of our investigation is an up to 20-fold increase in performance of an acid anhydride cured epoxy resin with respect to partial discharge endurance. The high endurance is obtained by a dispersion of nanoparticle silicon dioxide Aerosil in the epoxy system. Although there is a certain spread in the observed endurances, this does not mask the observation of an increase in endurance as the Aerosil content is increased up to the limit of workability. A replacement of half of the Aerosil by nanoparticle anatase appears not to influence this finding. Moreover, the high level of endurance is maintained by a coarse-particle filling with dolomite of an epoxy phase containing both Aerosil and anatase.

Acknowledgments

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Appendix

This is a more extensive description of the experimental steps of section 2.

A.1. Polymer plate specimen preparation

All specimens for the present work are cast in a 1 mm gap between two steel plates measuring 10 × 100 × 100 mm. Each of the steel plates is diagonally provided with two 6 mm threaded screw holes, one in each of two diagonal corners. The holes make it easier to separate the steel plates when the casting is being released from the mould. The steel plates are fine grain alloy steel, HB = 320, ground and polished to mirror like finish and coated with Balinit A titanium nitride (Balzers Sandvik Coating). Prior to epoxy casting the steel plates are provided with a release agent Silicon Trennmittel EF 8 (Wacker Chemie) thinned with heptane. After drying in an oven the release agent is rubbed off in an area of about 30 mm diameter in the middle of the steel plates. This is because it is observed that release agent is only necessary at the edge of the casting where the epoxy system is in contact with air during curing. Inside the edge of the casting this epoxy system shows very little adherence to Balinit A.

One steel plate is placed horizontally and three 1 mm spacers are placed well apart on its surface. The second steel plate is placed on a balance and a quantity of the degassed bubble-free epoxy mix corresponding to 2.5 ml is weighed onto the plate, care being taken not to introduce air bubbles by this operation. When casting highly viscous mixes containing anatase and dolomite, bubbles cannot be seen. In these cases the steel plate is placed horizontally in a vacuum desiccator or chamber and the epoxy mix is given a final degassing.

Next the second steel plate in one operation is turned upside down and lowered in a controlled manner onto the first steel plate until it rests on the spacers. In this way the viscous mix will first hang down until it contacts the first steel plate whereafter it will be squeezed out in a 1 mm thick layer. The assembly is placed in an oven for curing of the epoxy mix according to the schedule in section 2 of the paper.

To cast more than one specimen at a time one can use a number of steel plates stacked with 1 mm spacers in between thus using both faces of a steel plate.

Release of the cast epoxy plate specimen from the steel plates is accomplished by placing the assembly in lukewarm water while still at about 50 °C, inserting two Allen screws in the holes and screw to separate the steel plates slowly. A thin brass strip inserted under a screw will prevent damage to the steel plates. Doing the separation in water dampens the vibrations of the epoxy plate at the moment where it disengages the steel, so that it will not fracture. The epoxy plate is rubbed gently with isopropanol on a towel in order to free it from any adhering release agent.

The preparation of the epoxy system and dispersion of particles deserve a few words:

(a) Pure epoxy system. DGEBA + MNA are weighed into a flat bottomed cylindrical powder glass (internal diameter = 35 mm, height = 100 mm), mixed, heated to 50 °C and degassed. When cold, BDMA is weighed in and mixed well into the fluid now forming the epoxy system. Prior to casting and curing the system is given a final degassing.

(b) Epoxy/Aerosil having up to 4 vol.% Aerosil. The same procedure is adopted as for the pure epoxy system. Then Aerosil is weighed in and dispersed in the epoxy system by exerting shearing forces. This is accomplished by repeatedly moving an 8 mm diameter round glass rod along the wall of the cylinder glass until all lumps have disappeared and the mass becomes soft as a sign of good dispersion. Prior to casting, the epoxy/Aerosil is given a final degassing.

(c) Epoxy/Aerosil having more than 4 vol.% Aerosil or containing anatase or both anatase and dolomite. A quantity of the degassed pure epoxy system is weighed into a wide mortar. The particle substances are added in small portions in the order Aerosil, anatase, dolomite. After each addition the mass is worked with a pestle until dispersed. The pestle is removed and the mass—still in the mortar—is degassed prior to casting. The epoxy/particle system does not flow readily and may even be thixotropic, which is why transfer to the steel plate must be done with a scraper, simply a curved piece of polythylene cut from a 0.2 mm film. The mass is degassed after transfer to the steel plate. This may be eased by having the plate heated to 50 °C and using a heated vacuum chamber.

A.2. Electrode preparation and specimen mounting

This is a slight modification of the procedure given by Tanaka *et al* [3].

HV electrode: A 5.6 mm steel ball is soldered on one end of a brass rod of diameter 4 mm and length 77 mm. The rod has a conical hole allowing the ball to rest on the edge of the rod. After polishing the ball and the soldered joint, followed by ultrasonic cleaning in ethanol, the brass rod is placed vertically with the ball downwards in a 40 mm diameter polypropylene Multiform (Struers) casting mould provided with release agent. The ball should be about 3 mm above the bottom. The mould is filled with Araldite CY 225 plus HY 925 (Ciba Geigy). This is precured at 80 °C for 6 h, released from the mould and post-cured at 130 °C for 15 h.

When cold the terminal faces of the Araldite cylinder are machined on a lathe. The terminal faces should be plane parallel and there should be about 0.5 mm thickness of Araldite at the ball end.

Next the Araldite at the ball end should be wet ground with first 180 and finally 800 grade carborundum paper on a rotating grinding machine (lab type, used for grinding objects for microscopy) care being taken in maintaining parallelism. Grinding is continued until the steel ball just appears with a diameter not exceeding 0.5 mm. At this point it is worth making an inspection of the surface by magnifying glass: if any fracture of the Araldite is observed or if it has disengaged the steel ball the electrode should be discarded as it will result in early failure by the PD test.

Specimen—HV electrode joining: The polymer plate specimen and the HV electrode are rinsed ultrasonically in ethanol, dried and assembled concentrically with Loctite. Just before assembly it is advantageous to blow softly by mouth to make them slightly humid for safer polymerization of the Loctite. One to three drops of Loctite are sufficient. A thin adhesive layer is obtained by exerting an axial load of 10 kg during the 5 min polymerization of Loctite. This is most easily applied by using the chuck of a vertical drilling machine in which the brass rod goes with a loose sliding fit. The use of a drilling machine also allows for exact axial and concentric line-up of the specimen relative to the HV electrode.

Ground electrode GR: This is an 18–8 stainless steel roundel, 9 mm thick, with a diameter of 60 mm. The edges are rounded to avoid edge discharges. The surface is plain, smooth machined on a lathe to an almost mirror-like finish. On the bottom face the GR carries a stub with a hole for an electrical connection.

Spacer: This is ring shaped, of outside diameter 44 mm, and internal diameter 38 mm, punched out of a 0.125 mm Kapton film. Burrs left from punching are removed by grinding the outer and inner edges with the aid of a small V-folded piece of grade 800 carborundum paper.

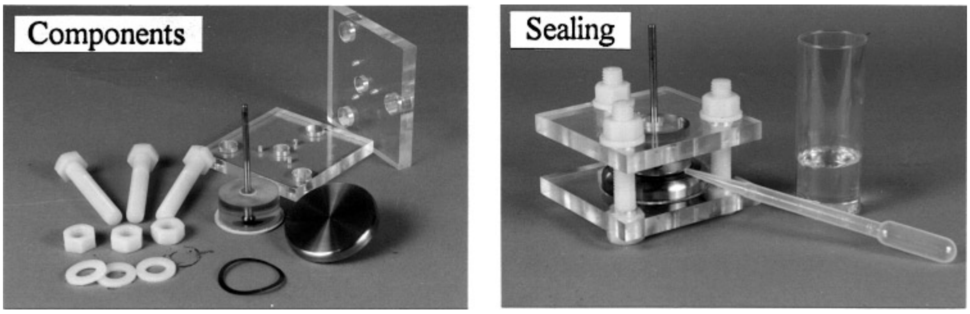

Figure A1. Left: the components of an assemblage (three bolts, nuts and washers, two acrylic plates, the specimen mounted on the HV electrode, the spacer ring and the GR electrode). Right: sealing the joint between specimen, spacer and GR electrode with a fluid epoxy mix Epofix by means of a pipette.

Assemblage: The spacer is inserted between the specimen plate and the ground electrode, these parts being clamped between two 10 mm arcrylic plates by means of three 12 mm diameter stay bolts made of Delrin. A seal of room temperature curing Epofix (Struers) is finally applied to hermetically close the joint (specimen plate–spacer–ground electrode). The assemblage is now ready for the PD test as shown in figure A1.

A.3. PD test

The 30 kV rms 50 Hz a.c. voltage used here is fed from a 1% stabilized 220 V mains via a variotransformer, an isolating transformer and an HV testing transformer. Five specimens can be tested in parallel. This is illustrated in figure A2.

The set-up was originally designed by Henriksen and Holbøll [11] for both endurance tests and discharge pulse pattern studies. The version used here for endurance studies has the following components marked with numbers on the diagram and photo:

1. Porcelain supporting insulator, 1 m high, electrical and mechanical fastening of the five HV fuses.
2. Five HV fuses, 50 mA.
3. Five silicone oil baths (acrylic), each with a specimen.
4. Capacitor, 1000 pF, $U_{\max} = 400$ kV.
5. HV testing transformer 440:100 000, rated output 5 kVA, style TEO 100/10 (Messwandler Bau).
6. Insulating transformer 1:1, 2 kVA.
7. HV meter ‘Scalamp’ electrostatic voltmeter, 40 kV rms max (W G Pye).
8. Resistor, wire wound, 187 Ω, forming part of the stiff tube connection from 4 to 1.

The flexible connections 5–4, 5–7, 2–3 are made of interlocking flexible metal hoses with a diameter not less than 12 mm to avoid corona. 1 and 4 are equipped with a metal tube ring in order to avoid corona from the edges of metal parts.

Human protection is afforded by having all equipment except for the variotransformer and the relay switch inside a grounded metal wire net cage. A door giving access to the cage is equipped with a contact interrupting the electrical supply when the door is opened.

The HV transformer 5 is protected from overload when breakdown occurs in a specimen by the 0.5 m long corona-free fuses 2. They are so designed that when a fuse wire operates, a

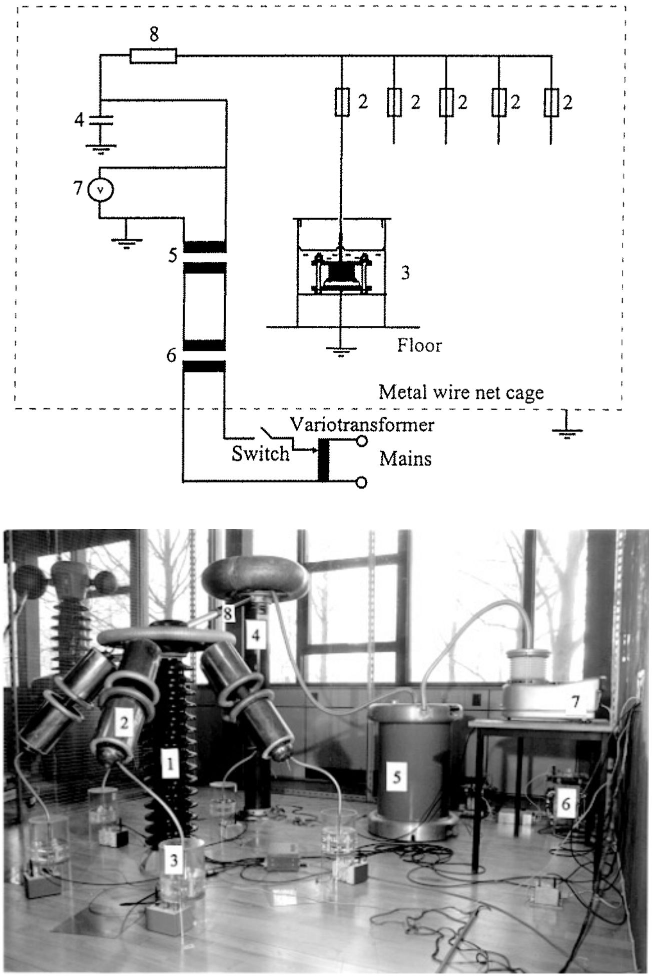

Figure A2. The PD test set-up. The numbers refer to the list of components on the preceding page. Top: diagram, bottom: photo of the set-up.

thin copper wire—held by the fuse wire and provided with a small load—will fall out of the fuse. The load lands on a grounded metal plate. The copper wire is long enough to maintain contact with the free end of the fuse. Thereby the HV electrode of the broken specimen is also grounded and continued sparking in the breakdown hole of the specimen is prevented. The relay switch operates at the same time, switches off the voltage for 5 s and switches it on again so that discharges will start again on the remaining unbroken specimens.

The endurance is the time from start of voltage application to when the fuse is observed to have operated.

The broken-down specimen is replaced by a new one by the following operation: the variotransformer is cranked down, the voltage interrupted by the door switch, the HV top of capacitor 4 is grounded with a grounding hook, the specimen is replaced by a new one already inserted in a clamping device, the fuse which operated is replaced with a repaired fuse, the grounding hook is removed, the door switch is closed, voltage is put on again and the variotransformer is cranked up until 30 kV is seen on voltmeter 7.

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