Nordic Insulation Symposium
Stockholm, June 11-13, 2001

Increasing the PD-endurance of epoxy and XLPE insulation by nanoparticle silica dispersion in the polymer.

Peter O. Henk
Technical University of Denmark
Department of Electric Power Engineering
Lyngby, Denmark

Thomas W. Kortsen
Elkraft System A.m.b.a.
Ballerup, Denmark

Thomas Kvarts
NKT Cables A/S
Brøndby, Denmark

Asghar Saeidi
Tornerosevej 73
Herlev, Denmark

Abstract

The endurance until breakdown by partial discharges (PD) has been measured using the Cigré Method II electrode arrangement. Two polymeric insulating materials - anhydride cured epoxy and crosslinked polyethylene containing nanoparticle amorphous silica (AEROSIL) in dispersion have been tested. The pure polymers showed endurances in the 100 to 200 h range. An increasing loading up to 5-6 pct vol. highly increased the endurance of both polymers to more than 2500 hours. By an additional 35 pct vol. loading of the epoxy with ordinary coarse fillers dolomite and quartz, the high level of endurance was maintained, while corundum reduced the endurance to almost zero.
Key words: Partial discharge; Nanoparticle filler; PD-Endurance; Cigré Method II.

1. Introduction

In the 1992 Nord-Is paper [4] it was indicated that dispersion of the nanoparticle amorphous silica AEROSIL in a MNA/DGEBA epoxy system not only gave an effect of reduced settling effect on coarse fillers, but also in itself gave an increased endurance against partial discharges, given by the accelerated PD-endurance test known as Cigré Method II.

These findings have since then been pursued and have resulted in test results on a number of polymers with and without fillers [1] [2]. This was done in consideration of polymers as important insulating materials in commercial electrical engineering where there is a risk of damaging PDs in voids and on surfaces of electrical insulation.

1.1. Materials investigated

The present paper concentrates on the results provided with the polymers widely used as electric insulation materials namely the polyethylenes: XLPE, LDPE, MDPE and epoxy: MNA cured DGEBA.

The nanoparticle fillers investigated are fumed Silica, AEROSIL and ANATASE of larger particle size. AEROSIL has been tested in the different polymers. ANATASE has additionally been tested in epoxy with the coarseparticle fillers: aluminiumoxide CORUNDUM, calciumfluoride FLUORITE, calcium magnesiumcarbonate DOLOMITE or siliciondioxide QUARTZ, this because ANATASE as an antisetteling effect on coarseparticle fillers [4]

We use the term nanoparticles when particle size is measured in nanometres rather than micrometres.

2. Experiment

The essential feature of the Cigré Method II PD endurance test used here is the establishing of PDs in a non-vented narrow airgap. This gap is between a plane metallic ground electrode and a one millimetre thick plate made of the polymer to be tested. The other side of the plate is glued to the plane face of an epoxy cylinder with an adhesive. The epoxy cylinder carries the high voltage electrode – a steel ball ground free in a narrow spot touching the adhesive layer as illustrated in figure 1.

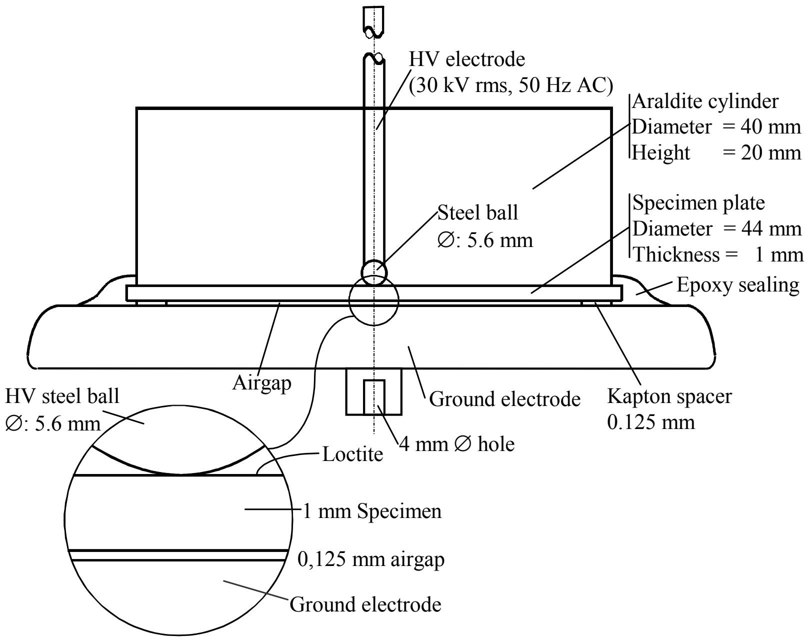

Figure 1. Cigré Method II. The specimen and air gap mounted between ball and plate electrodes.

The PDs are established by means of a 30 kV, 50 Hz AC supply. The endurance is the time in hours with PDs until breakdown.

The electrode preparation, the specimen mounting, and the PD test have been described previously in detail [1] and will not be treated here. The adhesive is normally Loctite.

2.1. Plate specimen preparation

The specimens can be divided into two groups: specimens prepared by the authors and specimens prepared by others. In the following the properties of the fillers and specimens made by others will be given.

2.1.1. Inorganic fillers:

	Density Kg/m^3	Particle size 10% - 90%
AEROSIL fumed silica (Degussa)	2140	7 nm [5]
ANATASE (Merck)	3900	<200 nm-370 nm
DOLOMITE (unknown origin, filler grade)	2860	6 µm-43 µm
QUARTZ (unknown origin, filler grade)	2620	1.0 µm-2.0 µm
CORUNDUM (white abrasives)	3950	5.2 µm-11.5 µm
FLUORITE (unknown origin)	3180	4.1 µm-48 µm

Table 1. Properties of the inorganic fillers.

In our term AEROSIL and ANATASE are nanoparticles and DOLOMITE, FLUORITE, QUARTZ and CORUNDUM are coarseparticles.

2.1.2. Polymers made into 1 mm plates by others:

(melt flow rate MFR, density d)
LDPE : MFR = 2.0 g , d = 920 kg m^{-3}
MDPE : MFR = 0.2 g, d = 935 kg m^{-3}
XLPE : MFR = 2.0 g of base polymer before X-linking by dicumyl peroxide, d = 918 kg m^{-3}, gel fraction = 82 pct,
All three polyethylene's containing Santonox R antioxidant, made both as pure polymers and with AEROSIL additive (NKT Cables A/S).
The XLPE is degassed after cross-linking to ensure that by-products from the cross-linking such as acetophenone are removed.

2.1.3. MNA-cured DGEBA epoxy plates.

1 mm thick plates are prepared by casting in a gap between two steel plates kept 1 mm apart by spacers according to the method previously described [1] [2].

The coarseparticle fillers are applied in a volumetric (v/v) concentration of 35 pct while the nanoparticles are included in the epoxy phase. The fillers are FLUORITE, CARBORUNDUM, QUARTZ, and DOLOMITE.

The epoxy composites contain in their epoxy phase nanoparticles on two levels: 4.73 pct v/v ANATASE and 2.36 pct v/v ANATASE plus 2.36 pct v/v AEROSIL. These last volumetric percentages being based on the epoxy phase.

The ANATASE in connection with the fluid epoxy system is interesting because it acts as an anti-settling additive preventing coarseparticle fillers from sedimentation while the epoxy is still fluid [4]. Thus no results for pure coarseparticle filler have been included since the results would be confused because of the sedimentation of the coarse filler that causes the test samples to bend, making the specimen mounting in the test cell difficult.

3. Results

The endurances in hours from the PD tests are presented in two groups: Pure and AEROSIL filled polymers table 2, and coarseparticle filled epoxy with either ANATASE or AEROSIL and ANATASE table 3.

3.1. PD-endurance for pure and AEROSIL filled polymers

	v/v AEROSIL									
	0	1	2	2.36	3	4	4.73	5	5.4	6
Epoxy MNA/DGEBA	**116**[1)]	108	312	497	548	517	**1070**[2)]	1248	725, 5×>**2000**[3)]	1414, 2695
XLPE	137,140, 205		221	288		295,335, 548	502, >6500[4)]			
LDPE	66,171		276	100		268,298	140			
MDPE	130,140		150	118,244		203,273	148			

Table 2. Endurances in hours for pure and AEROSIL filled polymers.

Notes: 1) Median value from 25 tests ranging from 55 to 214 hours.
2) Median value from 8 tests ranging from 306 to 1289 hours.
3) Five tests terminated before breakdown.
4) The specimen was still under test when this paper was submitted.

Three pure XLPE specimens where tested without degassing, thus containing aceto-phenone. The specimens showed endurances of more than 268 h, 900 h and 2200 h - all tests where terminated before breakdown [2].

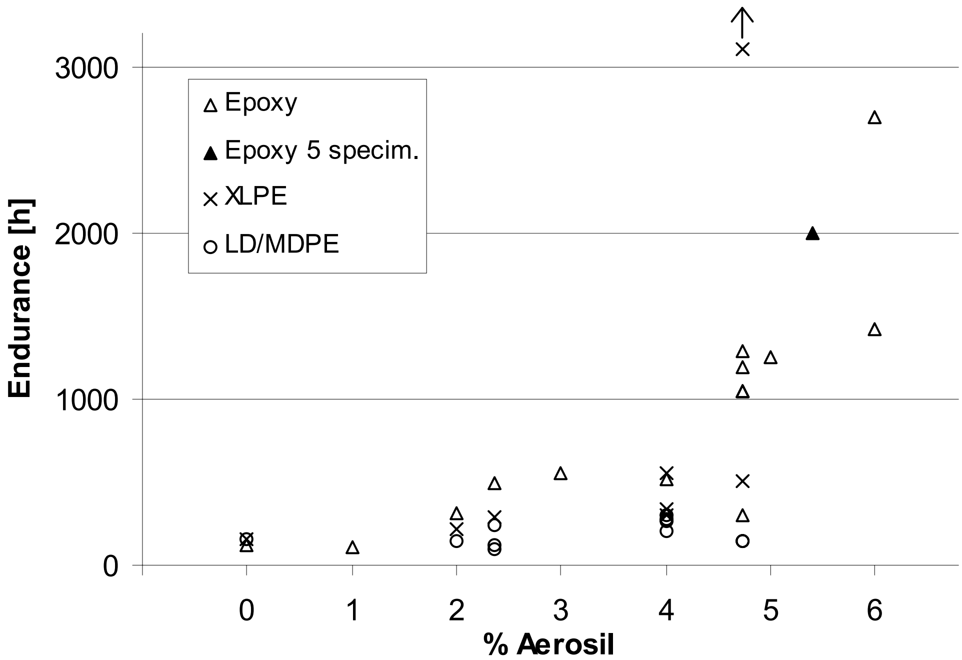

Figure 2. Endurances in hours for pure and AEROSIL filled polymers.

3.2. Coarse particle filled epoxy

Coarse particle filler: 35 v/v of total	Epoxy phase with: 4.73 v/v ANATASE	2.36 v/v ANATASE + 2.36 v/v AEROSIL
No Coarse filler	3,381,426,528,>528[1)]	263,1725
FLUORITE (CaF_2)	0	29
CORUNDUM (Al_2O_3)	0, 6	78, 123
QUARTZ (SiO_2)	0, 306	1608, 4704
DOLOMITE ($CaCO_3$,MgCO)	156, 164	420, 1813

Table 3. Endurances in hours of coarse-particle filled MNA-cured DGEBA composite. 1) These 5 results from [4] where obtained with 5 v/v ANATASE.

4. Discussion

The results from the PD endurance test will be discussed as follows: Pure polymers 4.1, AEROSIL filled polymers 4.2, and coarseparticle filled epoxy composites 4.3.

4.1. Pure polymers

From an examination of the results for the pure polymers in table 3 it is remarkable that they all show low endurances. Scarcely more than 200 hours by this test. There is hardly any difference between thermoplastics, LDPE and MDPE and thermosets, XLPE and epoxy.

An exception is the three pure XLPE specimens that where tested without degassing and thus containing acetophenone, these specimens showed very high endurances.

This improvement of performance of XLPE with acetophenone has been described previously, see for instance [6], but to our knowledge not in a Cigré Method II test set up, which is remarkable since the volume of the air gap is relatively large compared to the thickness of the specimens.

4.2. AEROSIL filled polymers

An examination of the results for the polymers with AEROSIL from table 2 shows a large difference between the thermoplastics, LDPE and MDPE and thermosets, XLPE and epoxy concerning their PD endurances: The addition of AEROSIL scarcely shows any effect on the LDPE and MDPE while it has a strong positive effect on the endurance of XLPE and epoxy.

There is no immediate explanation for this difference in PD endurance. The following is an attempt to explain this observation hypothetically [1].

A well dispersed nanoparticle filling with AEROSIL in low loading, i.e. 1 – 5 vol. pct, has two consequences regarding the intrinsic texture:

A narrow interparticle spacing of 20 – 8 nanometres.
A high polymer/particle interface area of 10 – 40 km^2 m^{-3}.

This makes it possible that the nanoparticles function as distributed heat sinks.

A reason for the difference observed here between the thermoplastics and thermosets could be found if the thermosets have a stronger adhesion than the thermoplastics to the surface of each AEROSIL particle. A stronger adhesion would enhance the dissipation of energy from the footpoint of each discharge through the polymer/particle interfaces in a direction away from the footpoint. The local puls-like temperature peak would not be so high and the polymer would endure the PDs for a longer period.

4.3. Coarseparticle filled epoxy

AEROSIL and ANATASE appear to be the nanoparticles capable of increasing the PD endurance of the epoxy. AEROSIL has a large effect. AEROSIL plus ANATASE have the additional effect of preventing the settling of coarseparticle fillers in the fluid DGEBA/MNA system while it cures.

Table 3 shows that among the coarseparticle fillers investigated FLUORITE and CORUNDUM are harmful to the PD endurance of an AEROSIL/ANATASE/ DGEBA/MNA system. Contrarily QUARTZ and DOLOMITE have the effect of maintaining the high level of PD endurance shown by this system.

Considering the high thermal conductivity of CORUNDUM and its high melting point, it is surprising that it shows low PD endurance. This would make sense if the epoxy system has weak adhesion to CORUNDUM (and FLUORITE) and strong adhesion to QUARTZ and DOLOMITE. A strong and lasting adhesion would further the dissipation of energy from the footpoint of each discharge via the polymer/particle interfaces. A weak adhesion, which fails, would create narrow spacings in the polymer/particle interfaces, i.e. cavities, with the risk of additional damaging discharges occurring in the said cavities.

4.4. Practical relevance

Considering the risk of unintended cavities being present in commercial insulation the result presented are of relevance for high-field application of polymer insulation where AEROSIL dispersion is feasible, i.e. cable accessories polymer supporting insulators in gas insulated systems, manoeuvring rods and other moulded electrical equipment.

5. Conclusion

The influence of a dispersion of nanoparticle silica AEROSIL in a selection of polymers has been investigated with respect to partial discharge endurance. The major conclusion from our investigation is that AEROSIL has a strong effect of increasing the endurance of thermosets (network) polymers XLPE and epoxies. In thermoplastics such as LDPE and MDPE AEROSIL has no effect.

When coarseparticle fillers DOLOMITE and QUARTZ are added to MNA-cured epoxy with AEROSIL the high level of endurance is maintained, while CORUNDUM and FLUORITE have the effect of strongly reducing the endurance.

As an unintended and positive sideresult it was found that XLPE containing acetophenone as a by-product form the cross-linking also has a very high endurance in the Cigré Method II PD endurance test.

Acknowledgements

The authors take pleasure in expressing their gratitude to Mrs. I M Procida of NKT Research Centre A/S for the preparation of the polyethylene plates. We whish to thank E Andersen, G Hvirgeltoft, J Larsen and O D Olsen for technical assistance.

References

[1] Henk P O, Kortsen T W and Kvarts T: "Increasing the electrical discharge endurance of epoxy resin by dispersion of nanoparticle silica". High Perform. Polym. **11** 281-296, 1999.

[2] Henk P O, Kortsen T W, Kvarts T and Saeidi A: "Electrical discharge endurance for some pure and nanoparticle silica filled polymers". Submitted for publication in High Perform. Polym, 2001.

[3] Kako Y, Watanabe S and Higashimura Y: "A New Test Method for Internal Partial Discharge Resistance of Insulation Materials". Electr. Eng. Japan **112** 17-25, 1992.

[4] Henk P O, Henriksen M, Holbøll J T and Javid Iqbal: "The Influence of Various Mineral Fillers in Epoxy Plastics on the Resistance to Partial Discharges" Proc. Nordic Insulation Symp. (Västerås, Sweden) (Trondheim: Tapir) paper 4.2, 1992.

[5] Wason S K: Handbook of Fillers for Plastics, ed H S Katz and J V Milewski (New York: Van Nostrand) p 176, 1987.

[6] Katz C, Eager Jr G S, Leber E R and Fischer F E: Communication AVI-5 in Proc. Jicable 84 127-134, 1984.