Nano Effects on PD Endurance of Epoxy Nanocomposites

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Epoxy nanocomposites were prepared and subjected to partial discharges (PD's) taking place in a rod-to-plane electrode system to investigate the effects of nanostructuration in epoxy resins. Specimens of the nanocomposites used contains nano layered silicate, nano silica of two sizes, nano titania, and mixture of nano and micro silica. Nano fillers are either surface-treated or not. Evaluation is made by erosion depth measured with a laser microscope. Major factors effective against partial discharges are represented by the two major phenomena, i.e. the nanometric segmentation of epoxy surface and the strong bonding between nano fillers and their surrounding epoxy matrices. Mechanisms are discussed in terms of a hypothetical multi-core model.

Keywords: *nanocomposite, polymer nanocomposite, advanced materials, partial discharge, PD resistance*

1. INTRODUCTION

A prosperous perspective can be drawn regarding polymers as electrical insulation and dielectrics [1, 2], if they are nanostructured with nano-meter fillers, which are called polymer nanocomposites or simply nanocomposites. They are certainly a descendant of colloid chemistry grown in 1930's, but from the standpoint of electrical insulation technology, they are good children of micrometer-size inorganic fillers filled polymers that are usually called filled resins. There is a Japanese proverb that blue comes from indigo, but is more blue than indigo. Likewise, nanocomposites come from microcomposites, but can be superior to the microcomposites.

Newly born composites are named nanocomposites at present, and are clearly differentiated from conventional micocomposites. One of the major reasons is that such nanocomposites are radically different in filler content and in the availability of their interfacial surface area from microcomposites. Filler content is 10 times smaller in nanocomposites than in microcomposites. There are interfacial regions between fillers and their polymer matrices. The former has enormous interfacial area as compared with the latter, i.e. roughly 10^3 times in the same content, and 10^2 times in the one tenth content. This big difference will cause significant change in various performances of polymer composites. It is reported in extensive literature that mechanical, heat-resistant, thermal conductivity, flame retardancy, gas barrier properties and the like as well as electrical and dielectric properties are much improved, if polymers are so nanostructured.

A general model was proposed to interpret various performances that nanocomposites exhibit as electrical and dielectric characteristics, which was called a multi-core model [3]. Above all, partial discharge resistance (PD resistance) was found to be drastically much improved, if polyamaide is nanostructured with clay or layered silicate [4]. Polyethylene also exhibit similar characteristics [5]. This paper deals with PD resistance of epoxy resin focusing on kinds, sizes, shapes, surface treatment of fillers to clarify the effects of interfaces, which are called nano effects. Such nano effects on PD resistance are interpreted in term of a multi-core model.

2. EXPERIMENTAL METHODS

Table 1 Base and Nanocomposite Specimens Evaluated

Symbol for Kind of Specimens	Filler Particles				Silane Coupling Treatment
	Nano Particle nm	Filler Content wt%	Micro Particle Silica μm	Filler Content Wt%	
N	Base	0	---	---	---
C	LS	5	---	---	no
S1	S 12	5	---	---	yes
S1n	S 12	5	---	---	no
S2	S 40	5	---	---	yes
S2n	S 40	5	---	---	no
S3	---	0	S 1.6	5	yes
S3n	---	0	S 1.6	5	no
T	T 15	5	---	---	yes
CFE	---		S 17	64.6	yes
NMMC2	LS	0.4	S 17	64.4	yes
NMMC10	LS	1.8	S 17	63.5	yes
NMMC(S1)	S 12	1.8	S 17	63.5	yes
Note : S: Silica, T: Titania, LS: Clay or Layered Silicate					

Base and nanocomposite specimens listed in Table 1 were evaluated on their partial discharge (PD) resistance. They included nano layered silicate, nano silica of two sizes, nano titania, and mixture of nano and micro silica [6]. PD resistance measurement was made by using a rod-to-plane electrode system as shown in Fig. 1. High frequency (720 Hz) voltage was applied to a 1 mm thick specimen with a 0.2 mm gap between a tungsten rod electrode of 1 mm φ with its tip radius 0.5 mm R and a brass plane electrode. The surface of the specimen was eroded by partial discharges taking place in the gap. High frequency voltage was used to accelerate such erosion. PD resistance was evaluated by the depth of erosion of specimen surface caused by partial discharges. The depth was measured with a laser microscope.

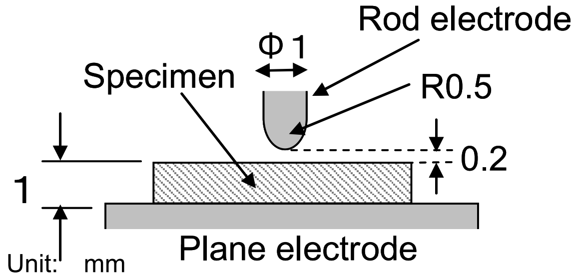
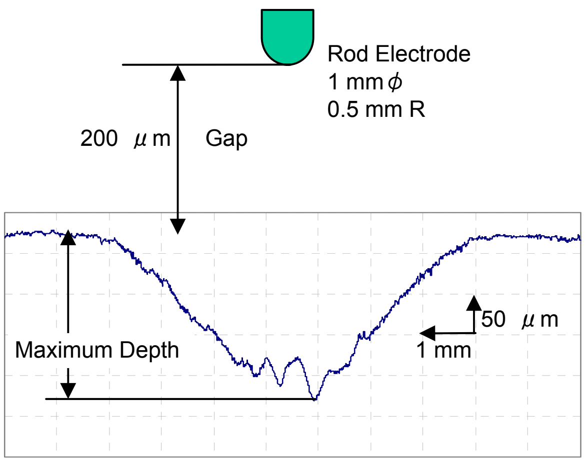


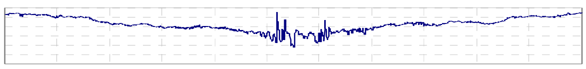
Fig. 1 A Rod-to Plane Electrode System to Evaluate PD Resistance of Flat Specimens

3. EXPERIMETAL RESULTS

3.1 Examples of Surface Erosion Profiles



(a) Base epoxy resin (N)



(b) Nano silica 5 wt% filled epoxy (S1)

Fig. 2 Examples of Erosion Profiles Aged in 60 Hz Equivalent Time of 1440 h under ac 720 Hz 4 kV

Surfaces are eroded for base and nano-filled epoxy resins, when they are aged during 120 h under ac 720 Hz 4 kV or during 60 Hz equivalent time of 1440 h as shown in Fig. 2. Erosion is cone-shaped and spreads over to the upper edge of about 0.5 mm in diameter, or ten times of a radius of the rod electrode in the both profiles. A big difference in erosion depth is recognized between the base epoxy and the nano-filled epoxy. It is worthwhile to notice that both the specimens are eroded, but the latter seems to form pits in the center area. It is interesting that erosion can be transformed into pit especially in nano-filled epoxy. Erosion depth in this paper is represented by the maximum depth in the cone for simplicity, by which PD resistance is inversely represented.

3.2 Effects of Kind and Size of Fillers on Erosion Depth

Erosion depth vs. aging time characteristics are shown in Fig. 3 for base resin (N), epoxy/titania nanocomposite (T), epoxy/layered silicate nanocomposite (C), epoxy/ silicate nanocomposites (S1 and S2), and epoxy/silica microcomposite (S3). It can be confirmed that there is a significant difference in erosion depth between the base resin (N) and the other nanocomposites, as already recognized in Fig.2. It is fair to state that addition of any kind of fillers will enhance PD resistance. Addition of 5 wt% micro-fillers does not make any significant contribution to suppress PD erosion, while that of 5 wt% nano-fillers contribute much.

There is a subtle difference among epoxy/titania nanocomposite(T), epoxy/layered silicate nanocomposite (C), and epoxy/ silicate nanocomposites (S1 and S2). Epoxy either with nano layered silicate (C) or with titania (T) seems to be a little bit inferior to epoxy with nano silicate. It might depend on the degree of homogeneity of filler dispersion, the strength of chemical and physical bonding, or filler shape (round, rectangular, or string).

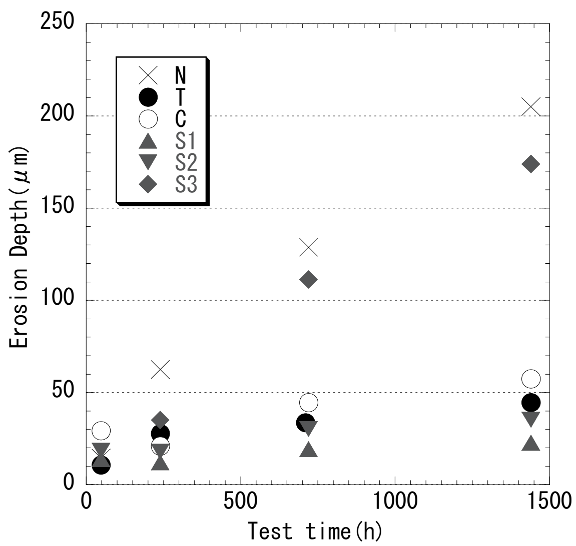


Fig. 3 Erosion Depth vs. Aging Time Characteristics as Filler Kind and Size Effect

There is a marked difference in erosion depth or PD resistance between epoxy resin specimens filled with same content of nano-fillers and micro-fillers (S1 & S2 vs. S3). A same tendency is also recognized in nano size region between two kinds of specimens with 12 nm and 40 nm in size (S1 and S2). More clearly it is interesting to analyze the dependence of PD erosion depth on the size of silica fillers at aging time 1440 h, as shown in Fig.4. There is certainly a size effect on erosion depth. The erosion depth is proportional to nearly n *th* (n=1/2 to 1/3) power of the size of silica fillers. Silane coupling treatment helps decrease PD erosion, and is more effective for nanocomposites than for microcomposites, as indicated by a dotted line and a solid line.

Filler size effect is an apparent phenomenon. Actually, regions between neighboring fillers are made narrower, as the size is smaller under the same content condition. The surface of polymers is segmented into many tiny areas, which can be called the segmentation. It is postulated as a working hypothesis for a surface erosion process or mechanism that segmentation of polymer surface by fillers will be effective to restrain PD erosion. Characteristics as shown in Fig. 4 will support such a postulated concept that the finer segmentation will make PD resistance stronger. Further, it should be stated that nanometric segmentation of the surface of epoxy resins by nano fillers is most effective against PD attack.

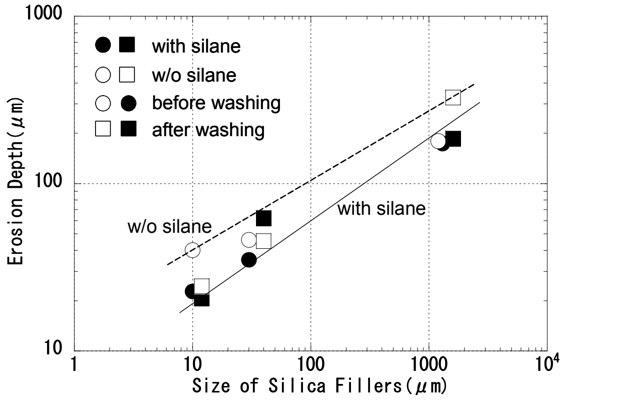


Fig. 4 Dependence of PD Erosion Depth on the Size of Silica Fillers at Aging Time 1440 h

3.3 Effects of Coupling Agent Processing on Erosion Depth

Figure 5 shows the depth of PD caused erosion as a function of aging time focusing on effects of interfacial state, i.e. on whether nano-silica fillers are surface-processed by coupling agents or not. Surface treatment or any resulted chemical bond will be effective to enhance PD resistance. It is also demonstrated in Fig. 4. Some knowledge can be drawn from comparison of erosion depth between two kinds of specimens with and without coupling agent processing (S1 and S2). Small but positive function seems to be working on to act against PD attack.

3.4 Difference in Erosion Depth between Nano Filled Epoxy and Nano-Micro Mixed Epoxy

Figure 6 shows comparative data of erosion depth at aging time 2880 h between conventional filled epoxy resins and nano and micro filler mixed composites. There in no clear difference recognized in erosion depth up to aging time 1440 h. At aging time 2880 h, it is observed that mixed composites are better than micro-filled epoxy, if filler content is appropriate. Nano silica as well as nano layered silicate will contribute to PD resistance in a certain degree. Increased segmentation is considered to be a reason for that.

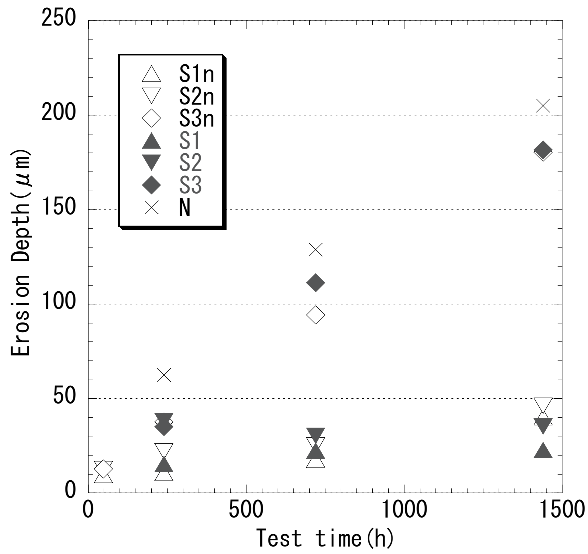


Fig. 5 Erosion Depth vs. Aging Time Characteristics as Interfacial Effects

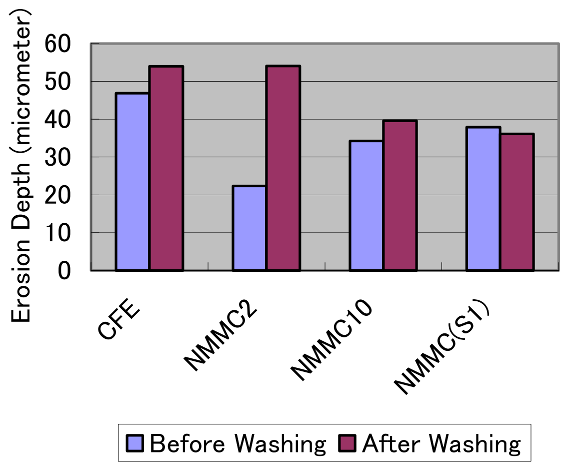


Fig. 6 Comparison of Erosion Depth at Aging Time 2880 h between Conventional Filled Epoxy Resins and Nano and Micro Filler Mixed Composites

3.5 Effects of PD Products on Measurement of Erosion Depth

PD products cover the surface of specimens to give scatter of erosion depth data. Such products are sometimes accumulated in pits formed by partial discharges. Ultrasonic wave is used to take them out. Data scatter due to product formation and other reasons can be seen in Fig. 7 as well as Fig. 6.

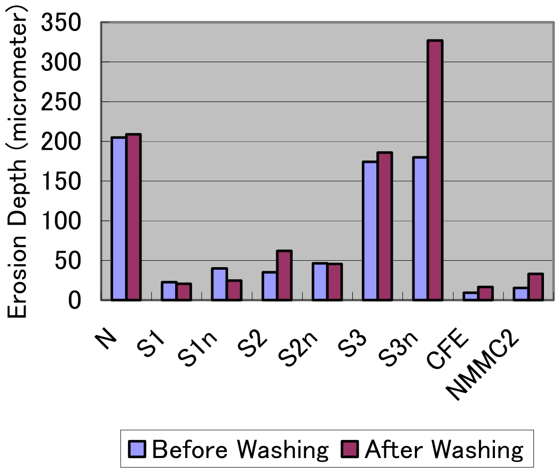


Fig. 7 Erosion Depth before and after Ultrasonic Wave Washing at Aging Time 1440 h

4. DISCUSSION

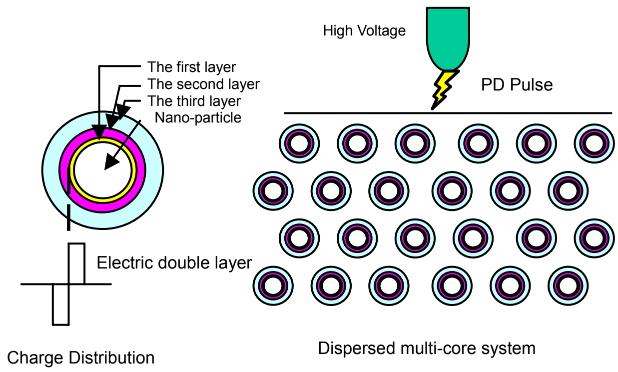


Fig. 8 A Multi-core Model to Interpret PD Resistance of Epoxy Nanocomposites

A multi-core model consists of the three layers in interfaces between nano particles and their surrounding polymer matrices. The first layer corresponds to the silane coupled regions, the second layer to stoichometrically crosslinked regions, and the third layer to less stoichioimetrically bonded regions. There is also a cooperative effect of many dispersed multi-cores considered.

PD resistance is enhanced by fine segmentation as the first predominant factor, as illustrated in the right part of Fig. 8. This can be explained simply by the very segmentation or division of epoxy resins. There may be some room to take some cooperative effect of the dispersed multi-cores into consideration. Electric double layers can make a certain contribution such as interaction with partial discharges, which needs further investigation. The second factor will be a contribution from the first layer of the multi-core model. Stronger bonding of the first layer will help increase PD resistance. It must form hard cores or layers working against violent PD pulses.

Partial discharges are rather violent to polymeric materials. Segmentation by multi-cores and hard core of the first layer are two major barriers against partial discharges. The second and third layers may work, but no clear contribution from them can be apparently recognized as far as PD resistance is concerned. They must be rather soft to withstand partial discharges.

5. CONCLUSION

There are two major factors working on as PD resistant functions. One is the fine or nanometric segmentation of the surface of epoxy resins provided by fillers. The other one is a function the hard cores of the first layer, i.e. silane coupled thin layer. Without hard cores, PD resistance will be diminished. The second and third layers and the electric double layer may work directly or indirectly, but there is no clear evidence for that at the moment, which leads to further investigation.

Individual findings are as follows:

(1) Epoxy nanocomposites exhibit excellent PD resistance. Nano silica gives better performances than nano layered silicate and nano titania.
(2) There is apparently a size effect on PD erosion depth in epoxy silica nanocomposite. The erosion depth is proportional to n *th* (1/3 to 1/2) power of size.
(3) Silane couplings are effective against PD's as the second factor.
(4) Nano filler addition to conventional filled epoxy will work to add more strength against PD's.

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