Dielectric Breakdown Strength of Alumina Filled Poly (ethylene-*co*-butyl acrylate) Nanocomposites

N. Jaeverberg¹, B. Venkatesulu^{1,2} and H. Edin¹

¹KTH Royal Institute of Technology
School of Electrical Engineering,
Stockholm, Sweden

²ABB CRC, Västerås, Sweden.

Abstract- Dielectric breakdown strength of poly (ethylene-*co*-butyl acrylate) (EBA) nanocomposites filled with spherical alumina particles was studied as a function of particle coating and relative air humidity. The nanocomposites were prepared from a mixture of EBA formulations (13 wt% butyl acrylate groups content) and alumina powder. The particles were either unmodified or surface-treated with aminopropyltriethoxy silane or octyltriethoxy silane. The filler content studied was 6 wt%. Every material formulation was thoroughly examined under SEM in order to verify homogeneous particle dispersion. Two different relative humidities of air were used for conditioning the samples prior to testing: 0 and 86 % RH.

The dielectric breakdown strength measurements were performed with a DC ramp of 1.2 kV/s. Ten samples were tested for each material formulation. Results were compared to the pristine EBA samples. Applying Weibull analysis to the measured data indicated a slight increase in breakdown strength for the dry nanocomposites filled with amino-treated particles as compared to the reference material in dry conditions. As expected, conditioning materials in humid environment had a negative impact on breakdown strength. This effect was more pronounced for nanocomposite materials, while the reference unfilled material was affected the least.

I. INTRODUCTION

Electrical breakdown strength (EBS) is one of the most important properties of any insulating material. It has been shown that the breakdown strength of common insulating polymeric materials can be improved by adding just a few weight per cent of nano-sized fillers [1 – 4]. Filler is said to be nano-sized if at least one dimension is below 100 nm [5]. The increase in EBS is attributed to the role of the interface between the nano-fillers and the host polymer matrix [6]. Achieving good dispersion of nanofillers in the host polymer matrix is one of the great challenges in manufacturing of nanocomposites; another issue is understanding the influence of surface modification of nanofillers on material properties.

In this study poly(ethylene-*co*-butyl acrylate) copolymer, with 13 wt% of butyl acrylate content is used as host matrix in expectation that polar butyl acrylate groups help to improve the particle dispersion. The matrix was filled with surface modified alumina nanoparticles with a size of less than 50 nm in diameter. Two different surface modifications were investigated in an attempt to understand its influence on dispersion and material properties. Due to time limitations only one filler content of 6 wt% was studied. In this paper these nanocomposites are studied with the help of a short-term

DC ramp test. The aim of this work is to understand the influence of the above mentioned surface modifications on the dielectric breakdown strength of the obtained materials.

II. EXPERIMENTAL METHODS

A. Materials

The nanocomposites were prepared at the Department of Polymer and Fiber Technology, KTH, from a mixture of poly (ethylene-*co*-butyl acrylate) copolymer (EBA), with 13 wt% of butyl acrylate content, aluminium oxide (Al_2O_3) nanoparticles (Nanodur, supplied by Nanophase, USA) and 0.2 wt% antioxidant Irganox 1010. A thorough description of the materials data and manufacturing process can be found in [7]. The base material was filled with either as received alumina nanoparticles ('U' materials) or after surface-treatment with either aminopropyl triethoxysilane ('A' materials) or octyl-triethoxysilane ('O' materials). In this study only materials with filler content of 6 wt% were tested. The alumina nanoparticles used were almost completely spherical with diameter < 50 nm according to the data from the manufacturer. Examining uncoated particles as received from manufacturer showed that the average particle diameter is ca 45 nm [8], see Figure 1.

Fig. 1 Nanodur alumina nanoparticles (SEM micrograph taken at the Department of Polymer and Fiber Technology, KTH)

B. Sample preparation and conditioning

Tape-shaped films were extruded first and then were further processed into films with thickness of approximately 140 μm by hot-pressing in vacuum conditions in the polymer press model TP 400 from Fontijne Grotnes. The hot-pressing was performed according to the procedure summarized in [7]. Thickness of the obtained films was measured with a digital micrometer model 227-221 from Mitutoyo with measurement

accuracy of 4 μm and measurement pressure set at 0.5 N. Finally circular samples of 3 cm in diameter were cut out with the help of a sharp scalpel. Twenty samples per material were produced – ten for the dry study and ten for the wet study.

All samples were dried thoroughly in vacuum conditions for 48 hours at about 50 °C, followed by 24 hours at about 60 °C prior to the measurements in order to remove trapped moisture. For the wet study the samples were conditioned in a desiccator in humid air at 86 %RH. The humidity was set by using a zinc sulphate heptahydrate salt solution (VWR International).

C. OIT Measurements

Thermal stability assessment was based on estimation of the concentration of effective antioxidant in the materials, which in turn was characterized by oxidation induction time (OIT) [9]. The comparison was based on initial OIT values for non-dried materials. The higher the values are the more thermally stable is the material.

Full description of the OIT measurements can be found in [9], here only a short summary will be presented. Mettler-Toledo DSC-820 was used for measuring OIT on unconditioned samples. This motivates comparison of the OIT data to the results obtained after conditioning in humid environment. The experiment was performed at 200°C in oxygen environment. Prior to the start of the measurement each sample was given 5 min to reach thermal equilibrium in nitrogen atmosphere. Two samples were used for each material. OIT data can be found in Table II.

Fig. 2 Modified measurement cell

Fig. 3 Experimental setup

D. Measurement setup

In this study for a progressive stress test a modification of a standard measurement method for evaluating breakdown strength of films and tapes [10] was used. The chosen rate of

voltage ramp was 1200 V/s, corresponding to reaching 60 kV DC voltage in 50 sec. The electrode diameter was kept at 6 mm with edge radius of 1 mm, but no weight criterion on the electrode weight was enforced. A drawing of the modified measurement cell used in this study is shown in Figure 2.

Measurements were performed with the experimental setup illustrated in Figure 3. Computer-controlled Hewlett Packard 33120A function generator was used for creating the input signal to the high voltage amplifier TREK 30 kV. The input signal sent to the TREK used in this study was a 70 Hz amplitude modulated sinusoid ramped from 0 to 10 V_{peak} in 50 sec. The DC doubler converted the HV TREK output to DC voltage of 60 kV DC voltage ramp across the sample. The voltage across the sample was registered by a Tektronix TDS3052 oscilloscope. Oscilloscope readings with 400 ms per division were retrieved by a computer and stored, allowing 50 sec sequence to be taken with reasonable time resolution. An example of the latter is shown in Figure 4.

Fig. 4 Example of a typical voltage across sample filled with amino-treated nanoparticles as measured by the oscilloscope

III. EVALUATION METHODS

A. Weibull statistics

Weibull distribution was chosen in this study as it is commonly used to analyze breakdown data of solid insulation [11]. It can be classified as an extreme value distribution, i.e. the system fails when the weakest link fails. A two-parameter Weibull distribution can be described numerically as shown in Eq. (1.1).

$$F(E, \alpha, \beta) = 1 - \exp\left(-\left(\frac{E}{\alpha}\right)^\beta\right) \quad (1)$$

where

E is the measured electric field strength at breakdown, $F(E)$ is the failure probability at an electric field strength less or equal to t ,

α is the scale parameter, the breakdown electric field at which the probability of failure is 0.632

β is the shape parameter, describing the spread in the breakdown electric field strength data.

The failure probability for each sample was calculated according to Eq. (1.2). Here n stands for the number of samples and i is the rank (between 1 and n) assigned to each sample after the breakdown electric field strengths were sorted in ascending order.

$$F(i, n) \approx \frac{i - 0.44}{n + 0.25} \cdot 100\% \quad (2)$$

Parameters α and β are estimated by rewriting Eq. (1) into a linear form, see Eq. (1.3).

$$\ln(-\ln(1 - F)) = \beta \cdot \ln(t) - \beta \cdot \ln(\alpha) \quad (3)$$

Parameter α is then used for comparison between different materials.

B. Error calculation

Error analysis was based on the estimation of a 90% confidence interval for the parameter α , which is estimated according to [11] by obtaining the lower and upper bounds for α as shown in Eq. (1.4). Values for Z_l and Z_u are obtained from the confidence interval tables (presented in Figures A.16 and A.17 in [11]) and are calculated using Monte-Carlo method with estimated accuracy of 1% for $4 < n < 20$.

$$\begin{aligned} \hat{\alpha}_l &= \hat{\alpha} \cdot \exp\left\{\frac{Z_l}{\hat{\beta}}\right\} \\ \hat{\alpha}_u &= \hat{\alpha} \cdot \exp\left\{\frac{Z_u}{\hat{\beta}}\right\} \\ \Delta\alpha &= \max\{|\hat{\alpha} - \hat{\alpha}_l|, |\hat{\alpha} - \hat{\alpha}_u|\} \end{aligned} \quad (4)$$

Fig. 5 Overview of breakdown strength data with the corresponding error bars for the nanocomposite materials and the reference unfilled material (please note the absence of the error bar for the 'A' nanocomposite is due to only 3 samples broke down)

IV. RESULTS AND DISCUSSION

The breakdown strength data is summarized in Figure 5 and Tables I and II. The following trends can be identified:

1. Dry 'A' nanocomposite is characterized by the highest breakdown strength among the tested materials (> 458 kV/mm). Only three samples out of ten broke down. This could be due to the highest silane coverage in comparison to the other nanocomposites, see Table I.
2. The differences between the breakdown strength values for the remaining nanocomposites and the reference unfilled material in dry conditions are very small. This probably should be expected considering the results obtained earlier from the dielectric spectroscopy measurements [7]. This was also found in the literature, e.g. for silica filled epoxy by Castellon et al. [12].
3. Conditioning the samples in a humid environment results in a reduction of breakdown strength. This should be expected as, for instance, it was reported that increasing humidity leads to increasing conductivity which in turn causes higher temperature rise at the breakdown point and consequently breakdown at lower fields [13]. The reduction in breakdown strength is more pronounced for the nanocomposite materials, while there is almost no change in breakdown strength for the reference unfilled material. Considering that the same amount of moisture was absorbed by the reference unfilled material as well as 'A' and 'O' nanocomposites (see Table II) and comparing the reduction in corresponding breakdown strength (see Figure 5) it can be argued that is in the case of nanocomposite material the water is absorbed into the interface between the nanoparticles and the base polymer material. This would result in more conducting areas around the nanoparticles leading to weakening of the interfacial area and lower the breakdown strength.
4. There seems to be a correlation between the breakdown strength of the wet samples (α_{wet}) and the thermal stability of the materials (OIT), as well as between the reduction of the breakdown strength after conditioning in wet environment and the OIT values, see Table II. Here, it is important to note the error margins for the OIT values, which is ± 2 min, resulting in almost the same OIT values for REF and 'A' samples. The thermal stability values are compared to the breakdown strengths for wet samples as materials studied in [9] were not thoroughly dried prior to the experiment. The trend for the higher breakdown strength for higher thermal stability of the materials is quite plausible as a breakdown is associated with local heat generation.
5. Comparing the scatter in breakdown strength data, calculated according to Eq. (1.4), it can be seen that the nanocomposite materials seem to be more predictable in comparison to the reference unfilled material, see Table II.
6. The 'U' nanocomposite is most prone to the influence of the absorbed moisture, which should be expected from the water absorption study, see Table II.

TABLE I
BREAKDOWN DATA FOR THE NANOCOMPOSITES AND REFERENCE UNFILLED MATERIAL

Material	α_{dry} , [kV/mm]	α_{wet} , [kV/mm]	β_{dry}	β_{wet}	Silane Coverage ^b [$\mu\text{mol}/\text{m}^2$]
REF	375	368	5.5	3.7	-
U	362	247	7.0	10.5	0
A	444 ^a	364	18.6	6.1	2.2
O	378	287	4.3	5.4	0.7

^aBased on only 3 samples

^bData is taken from [8]

TABLE II
BREAKDOWN DATA FOR THE NANOCOMPOSITES AND REFERENCE UNFILLED MATERIAL
COMPARED TO THE OXIDATION INDUCTION TIME

Material	α_{wet} , [kV/mm]	$\Delta\alpha_{wet}$ [%]	$\frac{\alpha_{dry} - \alpha_{wet}}{\alpha_{dry}}$, [%]	OIT [min]	Water Absorption ^a , $\times 10^{-4}$ [%]
REF	368	20	2	70	6
U	247	7	32	44	8
A	364	12	18	73	6
O	287	13	24	61	6

^aData is taken from [14]

V. CONCLUSIONS

It can be concluded that the 'A' nanocomposites had the highest breakdown strength in dry conditions among the materials studied. After the conditioning in wet environment the 'A' nanocomposites were also characterized by almost the same breakdown strength as the reference unfilled material. This makes it the most successful material formulation out of the materials in this study. This also indicates that the EBS of a nanocomposite can be increased in comparison to a reference unfilled material by using an appropriate coating of the nanoparticles (e.g. amino treatment in this study).

The differences between the breakdown strength values for the majority of the nanocomposites studied and the reference unfilled material in dry conditions are very small.

Conditioning the samples in a humid environment results in a reduction of breakdown strength.

There seems to be a correlation between the breakdown strength of the wet samples (α_{wet}) and the thermal stability of the materials (OIT), as well as between the reduction of the breakdown strength after conditioning in wet environment and the OIT values.

The nanocomposite materials seem to be more predictable in comparison to the reference unfilled material.

Materials filled with uncoated nanoparticles are most prone to the influence of humidity.

ACKNOWLEDGMENT

The project was funded by the Swedish Energy Agency, Elforsk AB, ABB AB, Swedish Railway Company, Ericsson and Borealis via the ELEKTRA program (grant 36028), and is gratefully acknowledged. Discussions with Dr H. Hillborg are gratefully acknowledged. Authors thank the department of polymer and fiber technology, KTH for the material manufacturing.

REFERENCES

- [1] J.K. Nelson, J.C. Fothergill, "Internal Charge Behaviour of Nanocomposites", *Nanotechnology*, Vol. 15, No 5, 2004, pp. 586-595
- [2] E. Tuncer, I. Sauers, D.R. James, A.R. Ellis, M.P. Paranthaman, A. Goyal, K.L. More, "Enhancement of Dielectric Strength in Nanocomposites", *Nanotechnology*, Vol. 18, No. 32, 2007
- [3] M. Takala, H. Ranta, P. Nevalainen, P. Pakonen, J. Pelto, M. Karttunen, S. Virtanen, V. Koivu, M. Pettersson, B. Sonnerud, K. Kannus, "Dielectric Properties and Partial Discharge Endurance of Polypropylene-Silica Nanocomposite", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 17, No. 4, 2010, pp. 1259-1267
- [4] M. Roy, J.K. Nelson, R.K. MacCrone, L.S. Schadler, C.W. Reed, R. Keefe, W. Zenger, "Polymer Nanocomposite Dielectrics – The Role of the Interface", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 12, No. 4, 2005, pp. 629-643
- [5] J.K. Nelson, "Overview of Nanodielectrics: Insulating Materials of the Future", *Electrical Insulation Conference and Electrical Manufacturing Expo*, 2007, pp. 229-235
- [6] T.J. Lewis, "Interfaces and Nanodielectrics are Synonymous", *International Conference on Solid Dielectrics*, July 5-9, 2004
- [7] N. Jäverberg, H. Edin, P. Nordell, S. Nawaz, B. Azhdar abd U.W. Gedde, "Dielectric Properties of Alumina-filled Poly(ethylene-co-butyl acrylate) Nanocomposites, Part I – Dry Studies", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 19, No. 2, 2012, pp. 383 – 390
- [8] P. Nordell, S. Nawaz, B. Azhdar, H. Hillborg, U.W. Gedde, "Preparation and characterization of aluminum oxide-poly(ethylene-co-butyl acrylate) nanocomposites", *Journal of Applied Polymer Science*, Vol. 125, Issue 2, 2012, pp. 975-983
- [9] S. Nawaz, P. Nordell, H. Hillborg, U.W. Gedde, "Antioxidant Activity in Aluminium Oxide - poly(ethylene-co-butyl acrylate) nanocomposites", *Polymer Degradation and Stability*, Vol. 97, No. 6, 2012, pp. 1017-1025
- [10] IEC 60243-1 "Electrical Strength of Insulating Materials - Test Methods", *International Electrotechnical Commission*, 1998
- [11] IEC 62539, "IEEE Std 930 - Guide for the Statistical Analysis of Electrical Insulation Breakdown Data", *IEEE Dielectrics and Electrical Insulation Society*, 2007
- [12] J. Castellon, H.N. Nguyen, S. Agnel, A. Tourelle, M. Fréchet, S. Savoie, A. Krivda, L.E. Schmidt, "Electrical Properties Analysis of Micro and Nano Composite Epoxy Resin Materials", *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 18, No. 3, 2011, pp. 651-658
- [13] P.W. Eka, T. Okazaki, Y. Murakami, N. Hozumi, M. Nagao, "Breakdown of LDPE Film under Heavy Water Absorption", *International Journal of Electrical and Computer Engineering*, Vol. 4, Issue 11, 2009, pp. 715-720
- [14] P. Nordell, "Aluminium Oxide – Poly(ethylene-co-Butyl Acrylate) Nanocomposites: Synthesis, Structure, Transport Properties and Long-Term Performance", Lic. Thesis in Polymer Technology, KTH, Stockholm, Sweden, 2011