

SPACE CHARGE ACCUMULATION IN EPOXY BASED MAGNESIUM OXIDE AND BORON NITRIDE NANOCOMPOSITES

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Abstract: A phenomenon that is typical in dc insulation is the accumulation of space charge which can significantly enhance the local electric field. This phenomenon is of special importance for polymeric insulation. Accumulation of space charge proved to be a limiting factor for HVDC applications. The goal of this paper is to show the different behavior of epoxy nanocomposites under various dc field strengths. Base material for all samples is commercially available bisphenol-A epoxy resin. Filler materials are MgO and BN with average primary particle size of 22 respectively 20 nm. It is shown that MgO filled epoxy resin has superior space charge behavior.

1. INTRODUCTION

Nanoscale magnesium oxide has already been shown to decrease the space charge density for high field strengths [1]. Boron nitride has good thermal conductivity, high breakdown strength and a reasonably high electrical resistivity. It has also been shown that BN in epoxy increases the glass transition temperature and dielectric constant, while not changing the dc conductivity or frequency dependence of the dielectric response much [2]. BN nanoparticles might be used to increase the thermal conductivity of epoxy while leaving the electrical properties intact. Space charge profiles of the two nanocomposites were obtained with the PEA-method and compared with each other as well as to neat epoxy. Possible explanations for the observed space charge behavior are given.

2. SAMPLES

2.1. Materials

All samples used in this study are based on commercially available epoxy resin (ER). The system consists of bisphenol-A type resin (CY231) and anhydrite hardener (HY925) from Huntsman. Filler material was magnesium oxide (MgO) with an average particle size of 22 nm and boron nitride (BN) with average particle size of 20 nm. For surface functionalization we used silane in form of γ -Glycidoxypropyltrimethoxysilane (GPS). Samples were prepared with filler loadings of 0.5%, 2% and 5% per weight. In case of BN-ER-composites only 0.5% and 2% samples could be created due to limitations stated below. Neat ER samples were used for reference measurement.

2.2. Particle properties

Both MgO and BN nanoparticles have been investigated with transmission electron microscopy (TEM). Micrographs of MgO nanoparticles showed that the

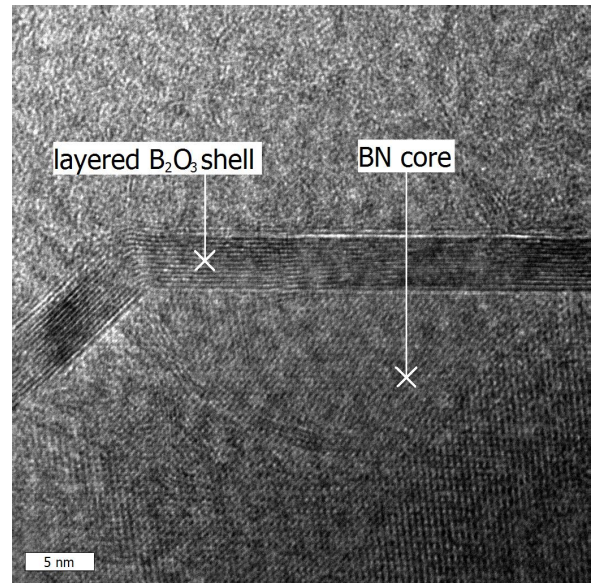


Figure 1. TEM micrograph of the edge of a BN-particle with clearly distinctive boron oxide shell.

crystalline particles have various shapes, being spherical, egg-shaped and in form of truncated cubes. The average particle size is 22nm with very narrow size distribution. The crystalline BN particles have two distinctive forms: spheres and truncated cubes. Further, BN particles exhibit a layered shell (8-10 layers) of 2,3 - 3 nm (see Fig. 1). This shell corresponds to boron oxide (B_2O_3).

2.3. Sample preparation

The samples were successfully fabricated using in-situ polymerization for surface functionalized MgO and BN particles. As-received particles were dispersed in 96% ethanol by means of ultrasonification at room temperature. The pH-value of the solution was adjusted with formic acid to 4 for MgO and 3 for BN, to reach higher ζ -potential, so that agglomerates could be broken down more easily. This worked very well for MgO, problems occurred with BN (see below).

After breaking up the agglomerates the GPS was added and the suspension underwent further sonification to allow hydrolysis. The resin CY231 was added to the mixture and the obtained solution was stirred with a high shear mixer to disperse the particles in the resin. Afterwards the mixture was put into a vacuum oven at 90°C to evaporate the ethanol. Due to trapping of the ethanol molecules in the mixture this step took considerable time. The weight was constantly monitored to ensure that all of the ethanol was evaporated before introducing a curing agent to the mixture. Hardener was added and the resulting mixture stirred with a high shear mixer. Afterwards the mixture was degassed with a combination of vacuum and ultrasonification, in order to prevent voids in the final sample. The samples were then cast in Al-molds and cured at 140°C for 3 hours.

2.4. Problems with preparation

The preparation of ER with BN saw some problems. Crimp et al [3] showed that the stability of hexagonal BN in a suspension is dependent on the oxygen content. The layers of B_2O_3 on the surfaces of our BN-particles prevented stable suspension formation. Due to their weak ionization characteristics B_2O_3 decreases the double layer length of the particles, thereby lowering the barrier to agglomeration. BN with a high B_2O_3 content shows a significant ζ potential (ζ -60 to -80 mV) from pH 6-10. Even at pH 3 ζ is still larger than 25 mV. ζ potentials of stable, dispersed suspensions are typically greater than ± 25.7 mV. At lower pH than 3 we witnessed monopolymerization of CY231, making it impossible to go below pH 3. Due to these limitations the suspension of BN and epoxy was not satisfactory.

2.5. Particle dispersion

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to study the dispersion of the particles in the epoxy. Due to the problems of dispersing the BN particles we already expected agglomerations. In figure 2 a slice of epoxy with BN particles can be seen. We could find some agglomerates with a size between 100 and 500 nm. Therefore the BN samples can still qualify as nanocomposites but could also be called mesocomposites. The dispersion of MgO in epoxy was sufficient to be regarded as nanocomposite.

3. SPACE CHARGE MEASUREMENTS

3.1. Setup

The space charge profiles in this paper were obtained with the pulsed electro acoustic (PEA) method. The principle is described in e.g. [4]. Schematic representation of the setup is shown in figure 3. An external electric pulse is applied to the sample and induces a

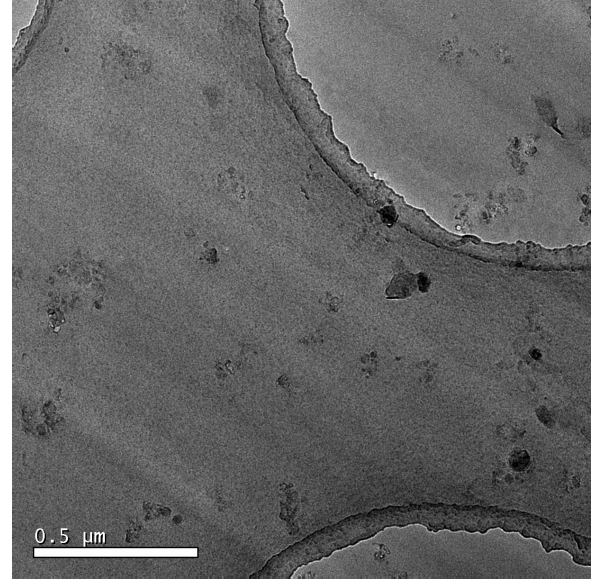


Figure 2. TEM micrograph of BN-dispersion in epoxy of a sample with 2 wt.% filler content.

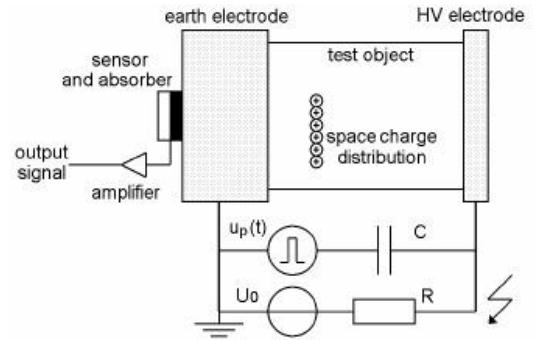


Figure 3. Schematic representation of the sample configuration and test setup for space charge measurements with the PEA method.

perturbation force on each charge. Due to this force the charges move slightly, consequently launching an acoustic wave proportional to the charge distribution in the sample. The acoustic wave can be detected and transformed into an electric signal by using a piezoelectric transducer.

3.2. Procedure

The measurement consists of three parts: calibration, poling and depoling. The calibration step itself is self explanatory. Poling was done for 1 hour by application of 10, 15 and 18 kV/mm with positive polarity. The duration of depoling depended on the sample, typically both MgO- and BN filled samples were almost charge-free in less than 1 hour.

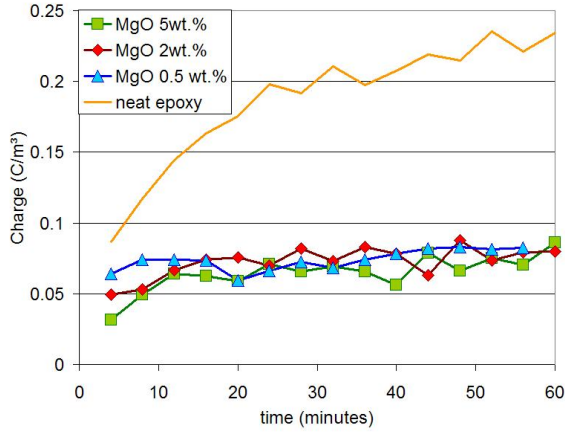


Figure 4. Growth of average space charge for MgO-ER-composites compared to neat ER.

4. SPACE CHARGE MEASUREMENT RESULTS

4.1. Space charge accumulation

Figure 4 shows the amount of space charge in MgO-ER samples compared to neat ER as a function of time. All MgO-samples had considerably lower space charge densities than the ER reference sample. After 1 hour of poling the amount of charges in the neat ER sample was three times higher than in any of the MgO-ER-composites. MgO also has faster charge dynamics. After less than 15 minutes MgO-ER samples reached their saturation point, while the neat ER sample was still accumulating charges. As seen in Figure 5 the BN-ER-composite shares the fast charge dynamics, but the amount of space charges is considerably higher. After 1 hour of charging the 0.5 wt.% BN-ER sample had double the amount of space charges that we witnessed in the reference sample, matters being worse with 2 wt.% BN-ER (Fig. 6). Compared to the other samples the 2 wt.% BN-ER-composite shows large amounts of space charges almost immediately after voltage application. For example, after 1 hour of poling at 18 kV/mm the amount of charges in 2wt.% BN-ER samples is 10 times higher than in neat ER.

4.2. Space charge profiles

Figure 7 shows typical space charge profiles for MgO-ER samples. We can witness some remarkable behavior between 15 and 18 kV/mm: the space charge density is reduced for higher field strength. At the earth electrode we see a relatively large amount of homocharge. The amount of charge increases from 10 to 15 kV/mm. But it decreases again when the field strength is further increased to 18 kV/mm. For 18 kV/mm the peak value at the earth electrode is 0.5 C/m^3 in 5% MgO-ER, compared to 1 C/m^3 for neat ER. This behavior also applies to the average amount of charge in the sample. An illustration of

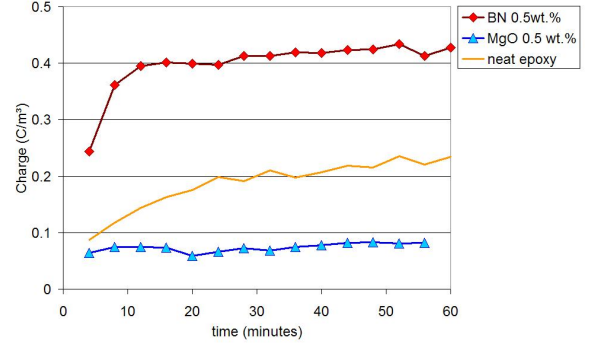


Figure 5. Charge dynamics of 0.5wt.% BN- and MgO-ER-composites.

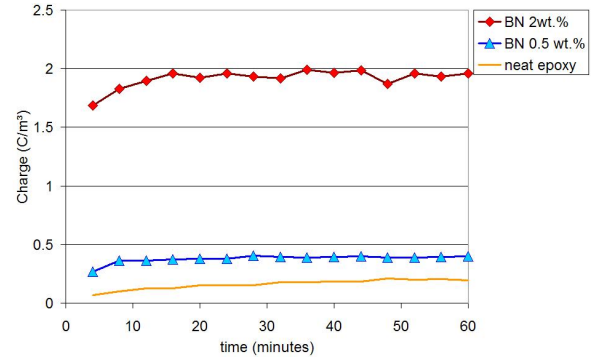


Figure 6. Growth of average space charge for BN-ER with different fillgrades for 15 kV/mm compared to neat ER.

this behavior can be seen in Figure 8. Furthermore the amount of space charge is drastically reduced for all MgO-ER-composites, compared to the neat ER. The homocharge peak at the earth electrode for the 5wt.% MgO-ER sample is with 0.5 C/m^3 at 18 kV/mm only half of the peak for neat ER at the same field strength.

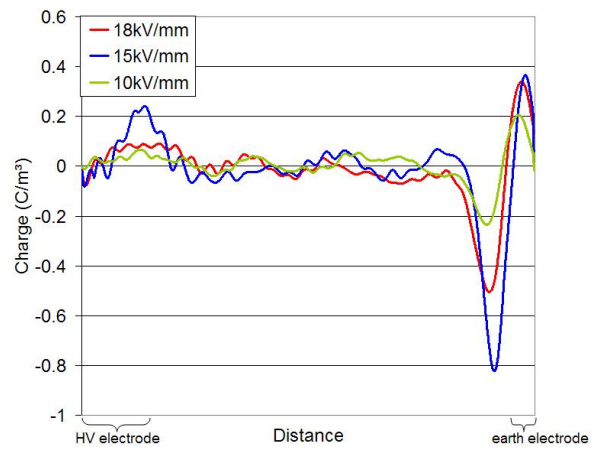


Figure 7. Space charge profiles for MgO-ER with 5wt.% fillgrade for different field strengths after 1 hour of poling, obtained with the PEA-method (voltage-off-profile).

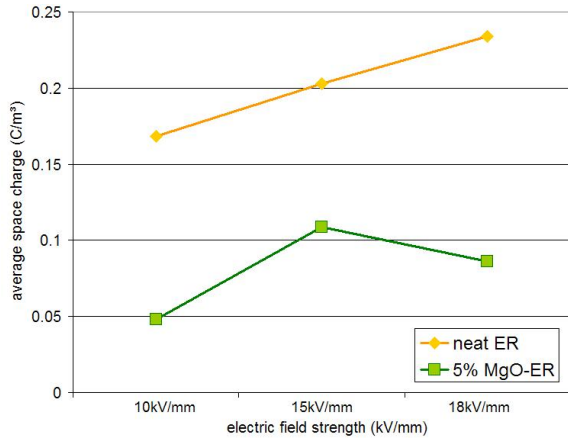


Figure 8. Average amount of space charge in 5wt.% MgO-ER after 1 hour of poling as function of the electric field compared to neat ER.

4.3. Depletion of space charges during depoling

Similar to the fast charging behavior we also see a quick depletion of space charges. The average amount of space charge in MgO-ER samples compared to the reference can be seen in Figure 9. All MgO-ER-composites were charge free in less than 30 minutes, having very low space charge densities almost immediately. BN-ER-composites showed inferior behavior. For example the 0.5 wt.% BN-ER was charge free after 40 minutes, sporting larger amounts of trapped charges than the reference sample most of the time (see Fig. 10). The BN-ER-composite with 2wt.% showed again the highest amount of space charges. For example after 1 hour of depoling it still showed 0.75 C/m³ on average, which is almost 40% higher than the peak value for the 2% MgO-ER-sample during poling with 18 kV/mm.

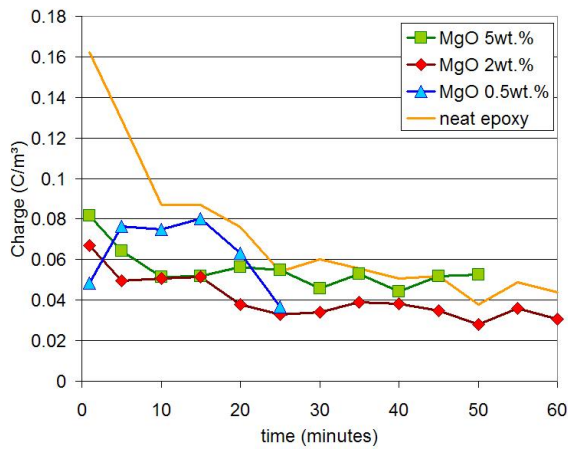


Figure 9. Depletion of average space charge for MgO-ER-composites compared to neat ER.

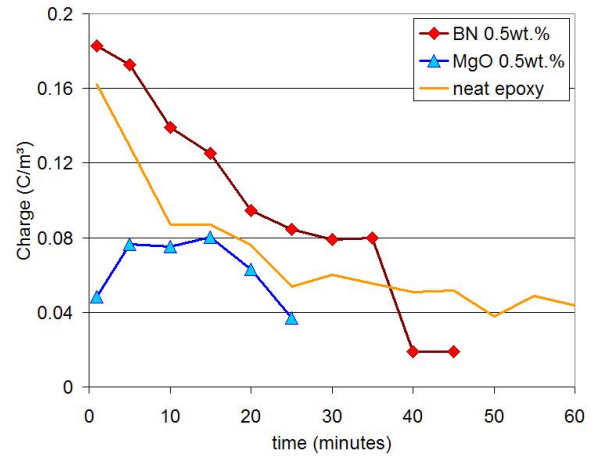


Figure 10. Depletion of average space charge for BN- and MgO-ER-composites with a fillgrade of 0.5wt.% compared to neat ER.

5. DISCUSSION

Looking at the space charge profiles it is obvious that the samples with nanoscale MgO-filler show superior behavior regarding space charges. All MgO-ER samples show drastically decreased space charge accumulation. After 1 hour of poling the amount of trapped charges for MgO-ER-composites is roughly a third of the amount in neat ER. Considering the charge dynamics we also see that for both poling and depoling MgO-ER reaches a stable end value after relatively short time, typically less than 12 minutes.

One very interesting behavior of MgO-ER-composites is the reduction of space charges for higher field strengths. The homocharge peak at the earth electrode was smaller for 18 kV/mm than for 15 kV/mm in the 0.5% and 5% MgO-ER-sample. In case of the 5% MgO-sample also the average space charge density was reduced. Future experiments will show if this space charge reduction also translates into a higher dielectric breakdown strength. We will also perform PEA measurements at higher field strengths to see at what point the homocharge peak will increase again.

BN was chosen for comparison because of its similar structure to MgO. But a high content of B₂O₃ on the BN-particle surfaces lead to inferior behavior in every respect. Main problem was that the preparation of samples was very difficult. Due to the B₂O₃-layer we did not succeed in creating stable suspensions, leading to some relatively large agglomerates of 100 to 500 nm in the samples. Future experiments will be done with BN-powder with higher purity to prevent this problem.

The BN-ER-composites showed very high amounts of trapped charges. In earlier work we already noticed a correlation between dispersion and space charge ac-

cumulation [5]. These measurements underline this possible connection, since the MgO-ER-composites with good dispersion showed superior behavior compared to BN-ER-composites with some agglomerates. These agglomerates could act as charge-traps, leading to the rather large charge accumulation we saw in the space charge profiles. But the agglomerates were not so numerous, so we didn't expect such large space charge accumulations. We assume that the impurities of the filler material, especially the large amount of boron oxide, is also a reason for the bad behavior of BN-ER samples in this case. What BN-ER does share with MgO-ER is the relatively fast charge dynamics during poling compared to the base resin. Both BN-ER- and MgO-ER-samples reach a saturation point after 10 to 15 minutes, while the base resin sees a steady increase of charges during the whole poling process. During depoling MgO-ER-composites show superior behavior, being charge free after 10 to 20 minutes. The base resin needs up to 1 hour for depoling. The BN-ER sample with 2 wt.% shows quite bad depoling behavior. For example at the depoling process after poling with 18kV/mm for one hour: even though the BN-ER sample loses roughly 60% of its charges in the first 10 minutes, it still has a considerable amount of charges left. After 1 hour of depoling the average space charge of the 2wt.% BN-ER sample is still 40% higher than the peak value of the MgO-ER-sample with the same fillgrade.

The reduction of space charges in MgO-ER composites compared to the neat epoxy could be attributed to the material changes due to the introduction of the filler material. Our surface functionalized MgO-particles are supposed to form multiple connections to the base polymer. Without the filler the hardener that we use can only connect two epoxy chains together, while one particle could connect many of them. Therefore we could assume that cross-linking occurs and the particles form a network of epoxy chains, compared to the linear base polymer.

6. CONCLUSION

The space charge accumulation of epoxy based nanocomposites has been investigated with the PEA method. Two different crystalline filler materials have been used: magnesium oxide and boron nitride. The quality of the dispersion was validated by means of electron microscopy. Samples with boron nitride filler showed a few agglomerates of up to 500 nm. Therefore they can still qualify as nano-, but also be categorized as mesocomposites. Samples with nanoscale MgO-filler sport superior space charge behavior. The BN-epoxy-composites show increased charge accumulation. We assume that the impurities of the BN-powder used, especially the high boron oxide-content, are the main reason for the increased amount of space charges. The combination of space

charge and TEM results suggest that the quality of the particle dispersion also has an influence on the space charge behavior of the nanocomposite. The BN filled samples which showed more agglomerates also showed increased charge accumulation, while MgO filled samples showed a drastic decrease. This suggests that agglomerates of nanoparticles act as charge traps.

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