EPOXY RESIN WITH ALUMINIUM OXIDE NANOFILLER AND ITS DIELECTRIC PROPERTIES

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Abstract: Topic of this paper is dielectric properties of epoxy resins, containing nanoparticles of Al_2O_3. Dielectric spectroscopy was used during epoxy nanocomposite diagnostics. These new materials are candidates for use in manufacturing modern insulators, where it can aid in reducing their dimensions. This research also focuses on studying dielectric properties of Al_2O_3 nanofiller over long periods. Large number of nanoparticles and area between them in epoxy matrix means higher number of weak spots, which may be the source of defects and may lead to increased deterioration of nanocomposites compared to composites without nanoparticles.

Keywords: epoxy resin, spectroscopy, relaxation, diagnostics, Al_2O_3 nanofiller

1. INTRODUCTION

Constantly increasing requirements on size reduction of electric devices as well as also improving its parameters makes manufacturers to improve electric insulation of their products. For example, replacing SF_6 insulation system on 66 kV distribution grids or increasing their operational voltage. One of the proposed solutions [1], [2] is based on replacing SF_6 with a combination of vacuum and solid insulation made of nanocomposites containing epoxy and nano- and microparticles. Currently, properties of these particles are subject of intense research, but despite that, their life expectancy and stability are still not well known. This is most unfortunate, because applications of these materials count with 20 – 30 years of operation. Electrical insulating composite with nanoparticles contains, regarding their structure, large amount of interfaces, which in long-term view could be a source of problems. The goal of our research is long-term study of dielectric properties, which can be simulated by accelerated ageing at high temperatures.

2. PRESENT STATE AND BACKGROUND

The subject of our research is epoxy resins containing non-conducting Al_2O_3 nanoparticles. Material samples were acquired from Department of Electrotechnology of Faculty of Electrical Engineering and Communication, Brno University of Technology. Samples were cast in a special mould supplied by ABB Brno. During the process of sample manufacturing, epoxy, hardener, softener and hardening accelerators were mixed together in correct ratio (weight). The resulting mixture was heated and mixed at 60 °C, so the epoxy did not harden and was more viscous, resulting in smoother flow into the mould. Weight of the whole epoxy system was approximately 350 – 500 g and the ratio of nanoparticles was set to 3 %. As soon as the nanoparticles were added, they reacted in the epoxy, creating small clusters accompanied by air bubbles. By this, the filler increases its density and must be degassed. First, nanoparticles are mixed mechanically with the epoxy, followed by ultrasonic mixing for 10 – 30 minutes. Having been degassed, the mixture enters the first hardening stage lasting 3 – 4 hours at 90 – 110 °C. Once the mixture has a rubbery consistency, the mould is disassembled, the samples are removed from the mould and prepared for hardening in the second phase, so they can be used in electrode system. The second stage lasts 10 –

12 hours at 140 °C. Nanoparticles used in the process were supplied by Sigma Aldrich; manufactured using calcination. Purity of the supplied material was 99.2 % and average size of a nanoparticle was 15 nm. The supplier also guarantees that the diameter of nanoparticles will not exceed 50 nm. Dimensions of our nanocomposite samples were 2.5 x 30 x 2 mm. This batch of samples was too thick for dielectric measurements. Another batch was made using a different mould – thickness of these did not exceed 1 mm and they had capacity at least 20 pF. Samples were coated with graphite or silver electrode paste. Several different attachments of samples to measurement equipment were possible. First of all, samples were inserted into Novocontrol holder and analyzed by standard Novocontrol Alfa A analyzer, with frequency range 0,4 μHz – 40 MHz.

Figure1: Novocontrol Alfa-A Analyzer – Example of attachment in Novocontrol Alfa A [6].

In the second case, samples with contacted or sprayed electrodes connected to cold head of cryostat and each sample had thermal contact with the cold head. This mechanical attachment to the head has several advantages – most important being the simplicity of the attachment of different samples in cryostat, so it is not necessary to create contact surfaces using graphite or silver paste. Because the heated sample is subjected to cold of slightly warm nitrogen, it is important that the thermal contact is as good as possible. Terminals from electrode system are connected via BNC cables to Novocontrol Alfa-A analyzer. The control PC managed the whole measurement, including temperature control, so that the influence of the environment on measurement was minimized [4].

3. EXPERIMENT AND RESULTS

Results obtained from Novocontrol Alfa-A analyzer were processed in MS Excel. Figures 2 and 3 show loss factor ε'' as a function of frequency. The graph clearly shows the impact of temperature changes from -125 °C (on the left) up to 125 °C (right).

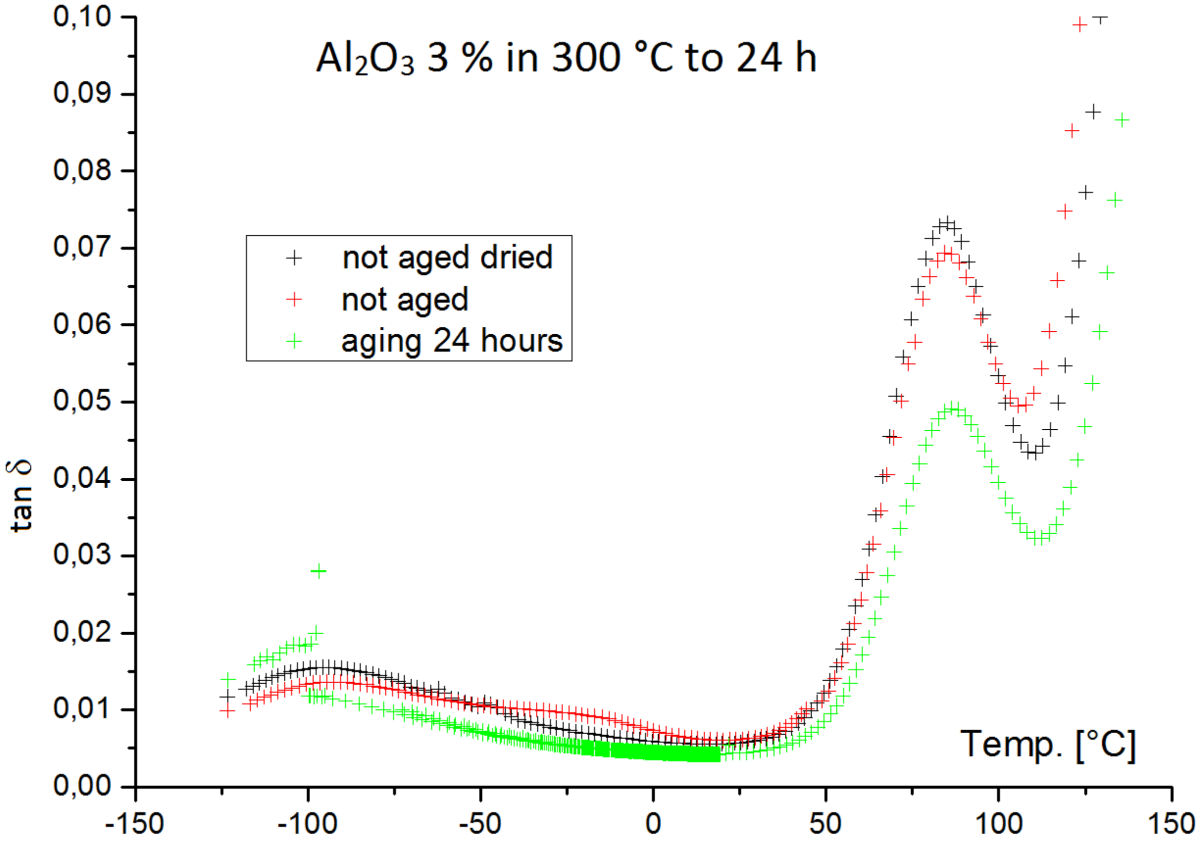

Figure 2: Al_2O_3 aged for 24 hours and drying.

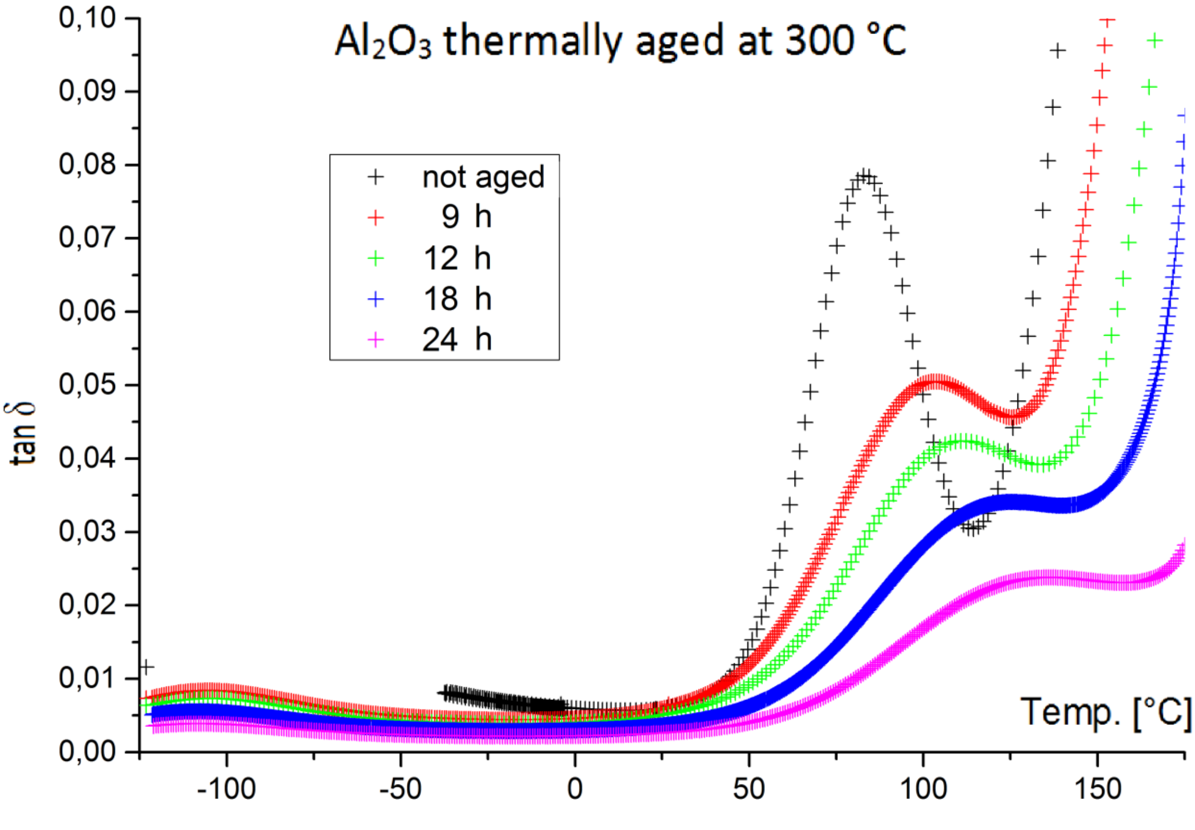

Figure 3: Tan δ dependence on temperature for epoxy resins with 3% Al_2O_3.

The influence of the temperature is clear. In case there are two relaxation mechanisms, the position of the β relaxation maximum is expected in the left part and α relaxation on the right side, before conductivity. The possible explanation might be a combination of several processes. The more probable explanation is incorrect temperature measurement, resulting in incorrect temperature data. Electric contacts of samples were correct, but thermal contact with cold head was insufficient. Thermal sensor was mounted on metallic holder, which was firmly connected to the cold head. Sample was stuck to the cold head using Apiezon H. Acquired data show that the temperature of the sample is not equal with the temperature measured by thermal sensor. This problem was solved, as shown in the following measurement. In similar fashion as the not aged sample in Figure 3, shows thermal dependency of relative dielectric constant (permittivity), which is a region between two relaxations. Discrepancy in thermal data can be observed at lower temperatures.

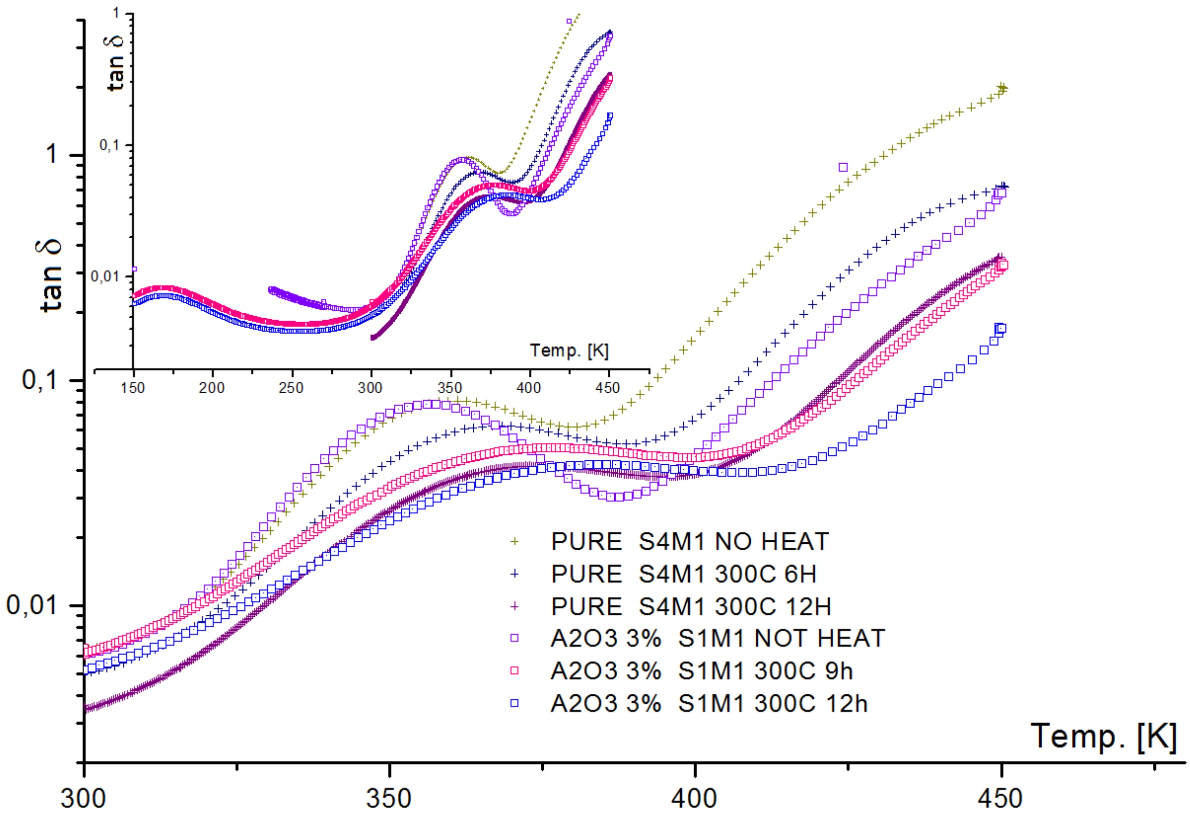

Figure 4: Tan Delta dependence on temp. for epoxy resins with 3% Al_2O_3 compared with pure epoxy.

Figure 4 shows six curves, the larger shows more detailed region of alpha relaxation, where it is also possible to observe changes and impact of the nanoparticles on the material. It can be seen that in the beginning, the maximum associated with the presence of nanofillers is more in the front than pure epoxy, but during the ageing process, the difference is reversed and further magnified. Finally, this maximum is 370 K for pure epoxy and 390 K for Al_2O_3 aged for 12 hours at 300 °C. Pure epoxy samples after ageing also show small maxima on the right in the conductivity area, but they were not subjects of our research. Another thing to mention is that not all samples were measured at subzero temperatures, mostly due to time required to measure and evaluate. The last anomaly is Al_2O_3 sample, which can be seen in region from 300 K and lower, showing considerable increase, which may have been caused by two factors. First, as published in [6], the author claims that there is a water peak which can be observed mostly on samples subjected to air and thus not properly degassed. The second option is a random error in Novocontrol system.

4. CONCLUSION

Observed dielectric spectra exhibit two relaxations and electrical conductivity is present. Thermal dependency of dielectric properties of nanocomposites was studied and measured. From measured data, we can conclude that maximum in the region of the α relaxation maximum, at which we observe shifts towards higher temperatures closer to conductivity, can show itself more clearly during the decrease of the magnitude of conductivity. One of the negative factors contributing to the data scattering might be the absence of uniform nanoparticle distribution in epoxy resin.

ACKNOWLEDGEMENT

This research was carried out under the project CEITEC 2020 (LQ1601) with financial support from the Ministry of Education, Youth and Sports of the Czech Republic under the National Sustainability Programme II.

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