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EXAMINATION OF THE PROPERTIES OF SAMPLES FROM GLASS-EPOXY CORE RODS FOR COMPOSITE INSULATORS SUBJECTED TO DC HIGH VOLTAGE

This article presents the results of an examination performed on a set of samples of glass-epoxy core rods used in composite insulators with silicone rubber housings. The goal of the examination was to test the aging resistance of the core material when exposed to Direct Current (DC) high voltage. Long term exposure of a glass-epoxy core rod to DC high voltage may lead to the gradual degradation of its mechanical properties due to the ion migrations. Electrolysis of the core material (glass fiber) may cause electrical breakdown of the insulators and consequently lead to a major failure. After being aged for 6000 hours under DC high voltage, the samples were subjected to microscopic analysis. Their chemical composition was also examined using Raman spectroscopy and their dielectric losses and conductance in the broad range of frequencies were tested using dielectric spectroscopy.

Keywords: DC high voltage, composite insulator, glass-epoxy core, dielectric spectroscopy, Raman spectroscopy

1. Introduction

Optimization of the cost of electricity transmission is directly linked to reducing transmission losses and improving the reliability of high voltage power lines. Newly constructed power lines are equipped with modern composite insulators, whose advantages have been recognized in many regions of the world.

One of the most important advantages is that their hydrophobic surfaces effectively limit the development of leakage current during sedimentation of conductive particles from the environment. Moreover, the silicone rubber used to make housings for such insulators has the ability not only to regenerate their temporarily lost surface properties, but also to provide hydrophobic properties to the surface pollution. In addition, composite insulators are light weight and cheaper than ceramic and glass insulators. Currently, global experience with composite insulators is mainly associated with their operation at AC transmission and distribution lines.

Recent years have shown growing interest in the transmission of electrical energy over High Voltage Direct Current (HVDC) lines [1,2]. Unlike in AC lines, however, the electrostatic phenomena that occur in DC lines may alter the degradation processes, affect electric strength [3,4] and increase the accumulation of surface pollution up to four times in comparison to AC systems [5]. Moreover, in case of the DC polarization the ignition of concentrated surface discharges is not turned off as in the AC system where the voltage curve passes through zero [5]. This dangerous phenomenon can lead to deep erosion of housing. Long term exposure of a glass-epoxy core rod to DC high voltage may lead to the gradual degradation of its mechanical properties due to the flow of ion current. Electrolysis of the core material (glass fiber) may cause such insulators to break and consequently lead to a major failure of entire element.

This paper presents the results of laboratory examination performed to analyze the extent to which the aging process caused by the possible flow of ion current erodes glass-epoxy core rods made of ECR glass. Type E of glass is a special type of alkali-free glass designed for electrical application; CR means that the glass is resistant to corrosion.

2. Test objects

The research was focused on investigating the samples cut from a glass-epoxy core rod used in composite insulators. The samples – 26 mm in diameter and 10 mm in height – were exposed to 2 kV DC high voltage for 6000 hours (Fig. 1). Copper electrodes were glued to their front surfaces in order to facilitate proper contact with the electrodes of the measurement system. The assumed value of aging voltage was approximately twofold greater than the value of rated voltages in composite insulators. The average value of the electric field strength for insulators is about 1 kV/cm while the value for the samples in the test was 2 kV/cm. The properties of the aged samples were compared with those measured in reference samples.

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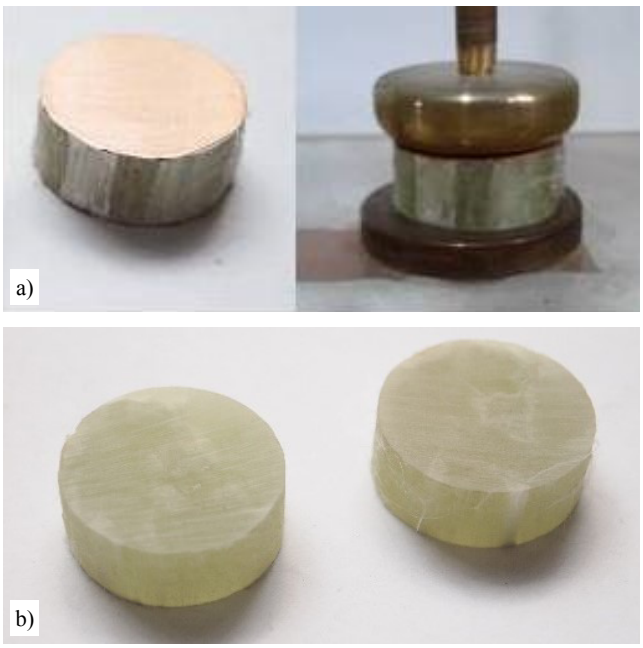

Fig. 1. DC voltage-aged samples of the material cut from the glass epoxy core rod of a composite insulator (a) and the reference samples (b). (Reference samples that were not aged, were not equipped with the thin copper electrodes)

Both the reference and the aged samples were analyzed using scanning electron microscopy (SEM) and Raman spectroscopy (RS). The test was designed to determine whether a long-lasting exposure to DC high voltage causes the glass-epoxy material of the core to show changes characteristic of a degradation process, i.e. electrical aging. It was expected that the material, especially the glass fibers, may undergo electrolysis. In such case, there might occur a flow of ions through the material, consequently followed by the movement of the mass.

The ionic leakage current, the concentration of ions and their discharges at the electrodes may cause permanent changes to the structure of the glass-epoxy material. The process may lead to the creation of some more or less branched current paths, going from the negative electrode, as well as some micro or even macro fractures. Other potential negative effects may include the occurrence of charred areas in the epoxy resin and deposits of the products of reactions of active atoms, which are created as a result of the neutralization of conducting ions on the electrodes (mostly the mobile Na^+).

Even one of the above described adverse effects of electrolytic aging would disqualify the analyzed glass-epoxy material from being used in the presence of DC high voltage.

3. Tests results

3.1. Microscopic examination

The microscopic examination was preceded by a thorough visual inspection of all the surfaces of both the aged and the reference samples. Copper electrodes were removed from the front surfaces of the aged samples. The detailed inspection, performed with a magnifying glass, showed no difference in the appearance of front and side surfaces between the aged and the reference samples. There were no visible traces – both on the front and side surfaces – indicating that the glass-epoxy material underwent electrolysis process. Therefore, the aged and the reference samples were subjected to comparative microscopic study using scanning electron microscopy with various magnification – between 100 and 500 times.

Already the initial inspection showed a large amount of scratches on all front surfaces, which were created when cutting the samples from the insulator's core rod. High heterogeneity of side surfaces was also observed. It should be stressed that both of the above mentioned effects were observed equally for the aged and the reference samples.

Fig. 2 shows the side surface of the aged sample, at the edge of the front surface – after removing of the positive electrode. The glass fibers are clearly visible – They have the diameter of more than 20 μm, are frayed and show multiplane weave. The same sample, rotated by 180°, shows at the edge of the same front surface only impressions left by the fibers that were torn from the epoxy resin – Fig. 3.

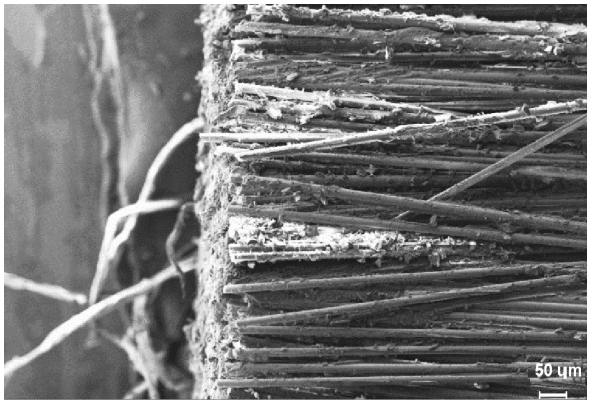

Fig. 2. Microscopic image of the side surface of the aged sample, with the edge of the front surface – after removing the positive electrode, 100 times magnification. Glass fibers have a uniform diameter of 21 μm and are slightly frayed

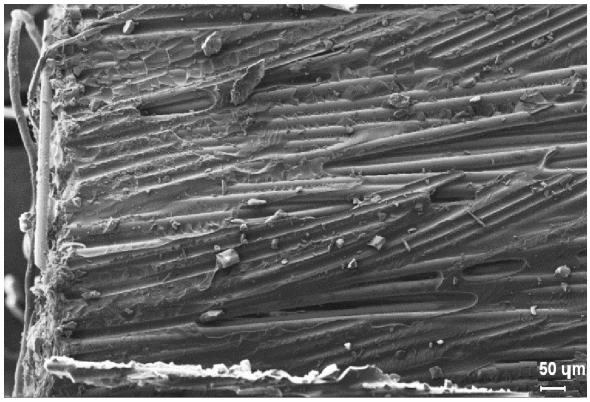

Fig. 3. Microscopic image of the side surface of the aged sample, at the edge of the front surface – after removing the positive electrode. 200 times magnification. Most of the visible elements are the imprints of the fibers broken away from the epoxy resin

Fig. 4 shows very similar area – at the edge of the aged sample's front surface on the side of the removed negative electrode. Both effects – slightly frayed fibers and impressions left by the broken away fibers are clearly visible.

The front and side surfaces of the reference samples, as shown in Fig. 5, have a similar appearance to the aged samples. Depending on the exact examined area, either more fibers or more impressions left by the fibers are visible. This is probably due to the mechanical process of removing the protective layer from the side surface of the insulator rod used as the source for the samples.

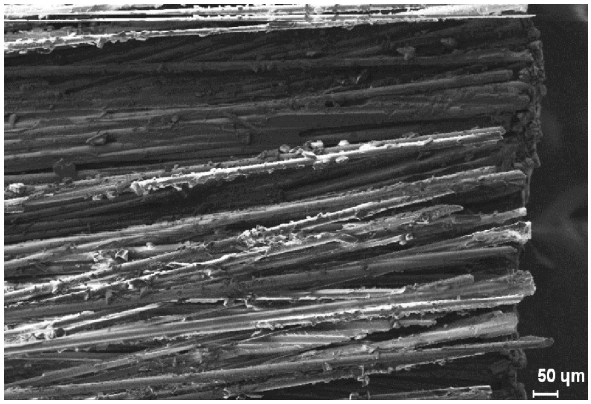

Fig. 4. Microscopic image of the side surface of the aged sample, with the edge of the front surface – after removing the negative electrode. 100 times magnification. The fibers – frayed to some extent – and imprints left by the broken away fibers are visible

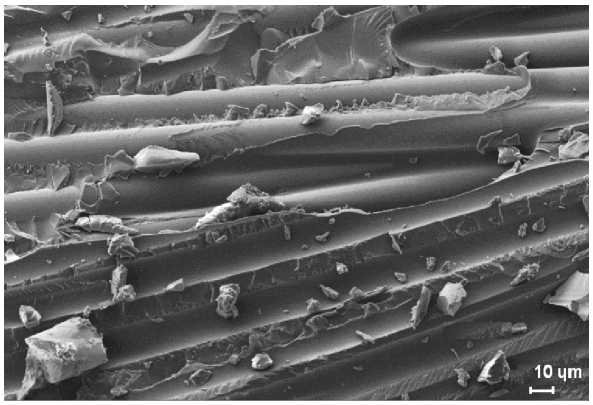

Fig. 5. Microscopic image of the side surface of the reference sample, magnified 500 times. The visible elements are mostly the imprints of the fibers broken away from the epoxy resin. Resin particles, small fragments of fibers and parts of the removed protective layer are of particular interest

An additional effect, observed in numerous spots on the side surfaces of both the aged and the reference samples, is the presence of a greater or lesser amount of resin particles, divided fiber fragments and parts of the torn off protective layer. The tearing and crushing of many fibers is most probably the result of removing the protective layer, as mentioned above. This effect is especially clearly visible in greater magnification – Figs. 5-7 – and results in a "mishmash" structure being created on the surface of the examined samples.

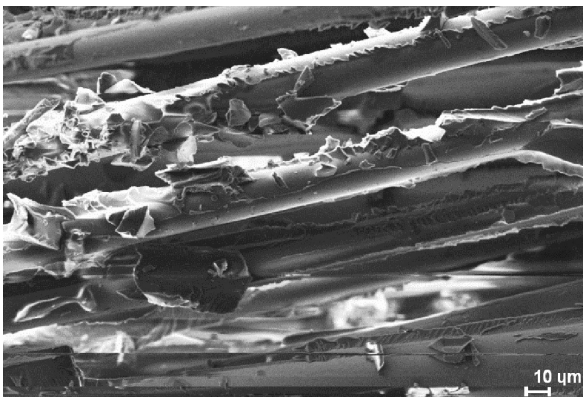

Fig. 6. Microscopic image of the side surface of the aged sample, magnified 500 times. Most of the visible elements are fiber imprints and the remainders of the removed protective layer

Fig. 7. "Mishmash" structure clearly visible on the side surface of the aged sample, magnified 500 times

Independently of the classical inspection and image documentation, an examination was planned using SEM EDS method (Energy Dispersive X-ray Spectroscopy). This was intended to recognize the spatial distribution of such element as: Si, Na, K, Ca – comprising the composition of the glass fibers. The examinations were intended to be performed in 8 points, beginning from the positive „+" electrode and towards the negative one („–" electrode). These tests, however, proved impossible to perform, due to high content of epoxy resin, which is an amorphous material. The presence of "mishmash" structure on the surfaces of the samples was an additional problem that practically precluded the SEM EDS tests.

Careful inspection of both front and side surfaces of the samples did not reveal any differences between the images of the aged and the reference samples. No effects were observed that could indicate degradation, especially electrolytic aging, in the aged samples.

3.2. Raman spectroscopy examination

Raman spectroscopy is an acknowledged method of analyzing the vibrational and rotational spectra of molecules based on the phenomenon of their polarizability during vibration. The

recorded spectrum allows the identification of functional groups and the chemical constitution of the samples under investigation. The comparison of the results obtained in the reference and the aged samples enables evaluation of degradation level of the latter.

By comparing the results for fresh material and for aged sample, it is possible to evaluate its degradation level. Even the slightest changes after a relatively short aging time may indicate a great threat occurring in a longer operating time-frame. Chemical changes may lead to a significant decrease in such parameters as mechanical strength and elasticity. Raman spectroscopy was already used in the analysis of the degradation level of the housings for composite insulators [6].

Raman spectra of the side surfaces of the samples were obtained using Renishaw workstation and Via Confocal Raman Microscope with Nd:YAG laser emitting at a 532 nm wavelength. Fig. 8 shows the measurement geometry for eight test points on the side surfaces of both the aged and the reference samples.

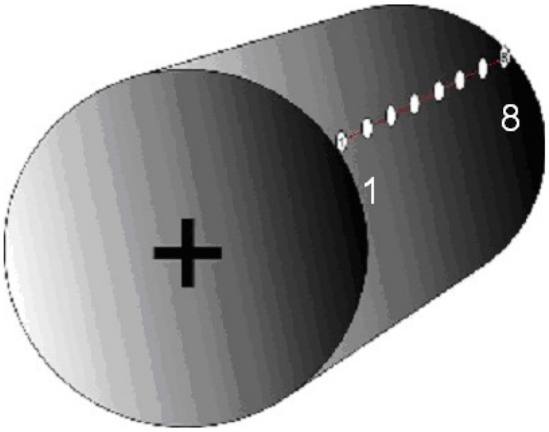

Fig. 8. The location of Raman spectra measurement spots on the side surfaces of the samples

If degradation (electrolytic aging) had occurred, it was expected to find spectral peaks evoked by chemical bonds containing of such elements as Na or K, or possibly from Ca and Si, which are present in glass. Their presence would be reflected in Raman spectra by strong and clear modes (peaks) in wavenumber ranges below 1000 cm^{-1} or possibly, in the case of simple salts, below 1200 cm^{-1}. By means of example, Fig. 9 shows the Raman spectrum of silicon with a strong peak of approx. 500 cm^{-1} and a weak peak of approx. 950 cm^{-1}.

In the case when degradation took place, the modes from the chemical bonds containg atoms (or ions) of the elements present in glass (below 1000 cm^{-1}) would show as additional peaks in the spectrum of the epoxy resin. Raman spectrum of typical epoxy resin has strong modes primarily in the range of 2700÷3000 cm^{-1} (including two very strong modes at approx. 2900 cm^{-1}) and weak modes in the range of 1400÷1700 cm^{-1}. Below this range no clear peaks occur.

As it was expected, the spectra recorded for the subsequent eight measurement points on the side surface of the reference sample were uniform. They were therefore averaged and represented in Fig. 10. The figure shows only weak modes, which

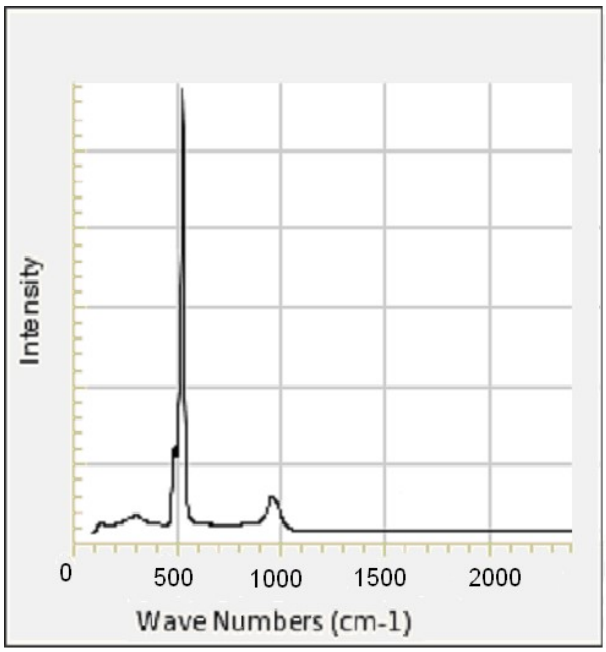

Fig. 9. Raman spectrum for silicon [7]

precisely correspond to peaks typical of those originating from epoxy resin. They are on a steeply increasing base line, whose shape is related to the photoluminescence phenomena in the glass-epoxy material, which comprises glass fibers. No peaks that would correspond to the elements present in glass occur.

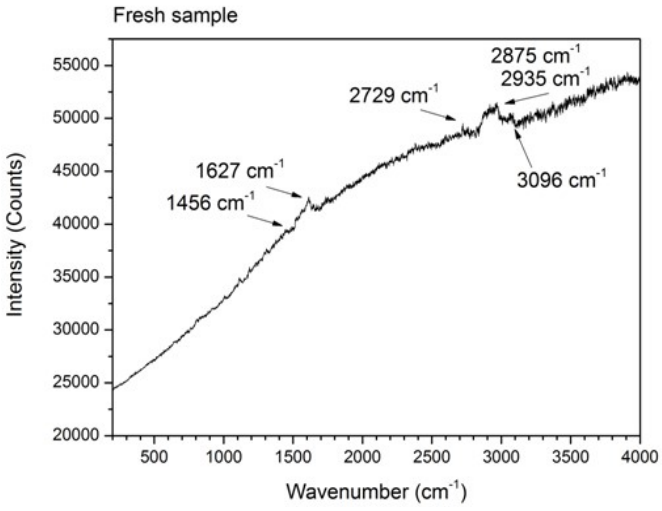

Fig. 10. The averaged Raman spectrum recorded for eight measurement points on the side surface of the reference sample

As in the case of the reference sample, no differences were found between the Raman spectra recorded for the eight points on the side surface of the aged sample. This confirms that no degradation took place as was indicated by the prior visual inspection and microscopic examination. The spectra recorded for eight measurement points on the aged sample were averaged and presented in Fig. 11. The spectra have no peaks that could origin from elements present in glass. This fact proves that electrolysis of the glass-epoxy material did not occur.

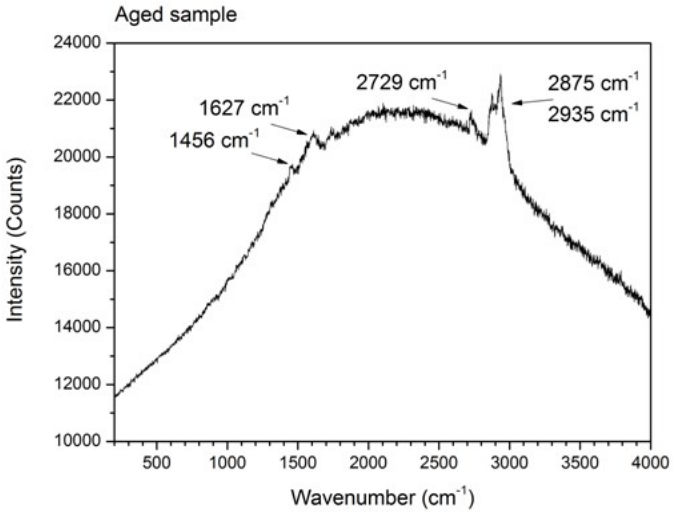

Fig. 11. The averaged Raman spectrum recorded for eight measurement points on the side surface of the aged sample

It was found, however, that the aged sample spectra are of different shape as the spectra of the reference sample (Fig. 10). The shape of the base line was of lesser importance from the point of view of the processes involved. Nevertheless, some differences were observed between the modes characteristic of epoxy resin.

The characteristic modes were indicated for the spectra of both the reference and the aged sample. The main and strongest mode (2800÷3000 cm^{-1}) comes from the vibrations in the carbon-hydrogen bonding (C-H), while the 3000÷3100 cm^{-1} range mode reflects vibrations in (=C-H) [8,9]. The mode in the range of 1680÷1820 cm^{-1} is characteristic of vibrations for carbonyl groups (C = O) [10,11]. The mode in the range of 1500÷1900 cm^{-1} is related to the vibrations of aromatic rings (C = C ↔ C-C), and the mode 1456 cm^{-1} results from the vibrations of nitrogenous double bonds (N = N), present in the analyzed system. As was mentioned above, both spectra did not show any bands (peaks) below 1200 cm^{-1}, which would come from the chemical bonds in glass fibers. Significant deviation of the base lines may be attributed to photoluminescence phenomena in the sample – related to the presence of glass fibers and the laser wavelength used.

The spectrum of the material from the aged sample differs from the reference sample spectrum by strengthening the main mode in the range of 2800÷3000 cm^{-1}. Additionally the 2729 cm^{-1} band is clearly enhanced. It corresponds to double carbon-carbon bonds (C = C). This fact may be explained as the effect of progressive, amplified polymerization of the epoxy resin. The increasing polymerization of resins due to the influence of electric and radiation fields is a well known and well described phenomenon [12-16]. Therefore – it is neither surprising nor connected to the deterioration of the properties of the resin. Conversely – its mechanical and electrical parameters may be increased, although the hardened resin becomes more brittle.

3.3. Dielectric spectroscopy examination

The examination was performed applying the effect that dielectric materials of heterogeneous structure placed in the electric field accumulate electric charges on their interfaces. Dielectric spectroscopy allows the measurement of the dielectric properties of the medium, based on the universal abilities of substances to react to external influence of the forcing field.

Voltage U_0 with pulsation ω applied to a sample in the form of a flat capacitor evoked the flow of current I_0 through the investigated medium. The current had the same frequency as the excitation voltage and is phase-shifted by angle ψ. The proportion between the voltage, current and phase angle is determined by the dielectric properties of the material sample (permittivity and conductivity) as well as by its geometry. This dependence takes the form of complex impedance Z or complex admittance Y:

$$Z(\omega) = Y(\omega)^{-1} = \frac{U(\omega)}{I(\omega)} = \left|Z(\omega)\right| e^{j\psi(\omega)} =$$
$$= ReZ + jImZ = Z'(\omega) + jZ''(\omega) \qquad (1)$$

In order to become independent from the geometrical dimensions of the analyzed material sample, it is possible to use material parameters resulting from the measured frequency characteristics of impedance or admittance. These parameters are complex values of electrical permittivity ε, complex conductivity σ and dielectric loss factor tgδ. The latter can be defined as $|\mathrm{Im}(Z)|/\mathrm{Re}(Z)$.

The measurements of electrical properties of cross-sections of prepared samples were performed with the use of the Alpha-A High resolution dielectric analyzer (Novocontrol). The frequency range was from 0.01 Hz to 10 MHz. During the measurements, the samples remained in the air atmosphere. Fig. 12 shows the frequency dependence (plot) for the tgδ factor of the fresh sample, for the sample aged for 3000 hours, and for the sample aged for 6000 hours. Although these plots do not demonstrate any relaxation processes over the investigated frequency range, they do indicate DC conductivity, as in the case of epoxy resin

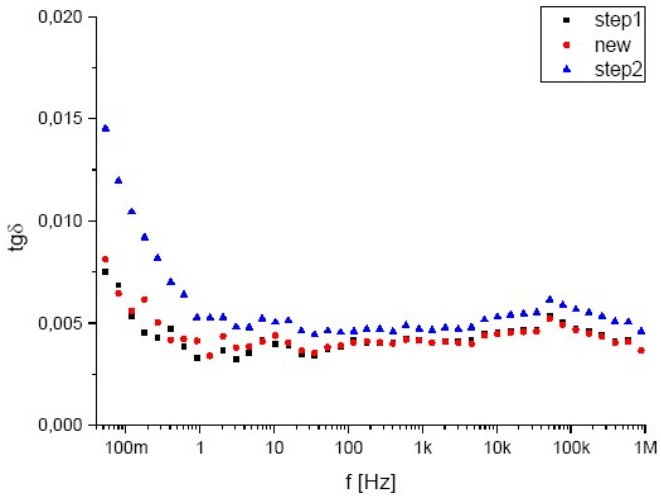

Fig. 12. Frequency spectrum of dielectric loss factor tgδ

reinforced with glass fibers [12]. However, the increase in the conductivity of the longer-aged sample is insignificant as compared to the fresh sample and to the shorter-aged sample. As shown in Fig. 13, a similarly insignificant increase in the AC conductivity is observed at low frequencies.

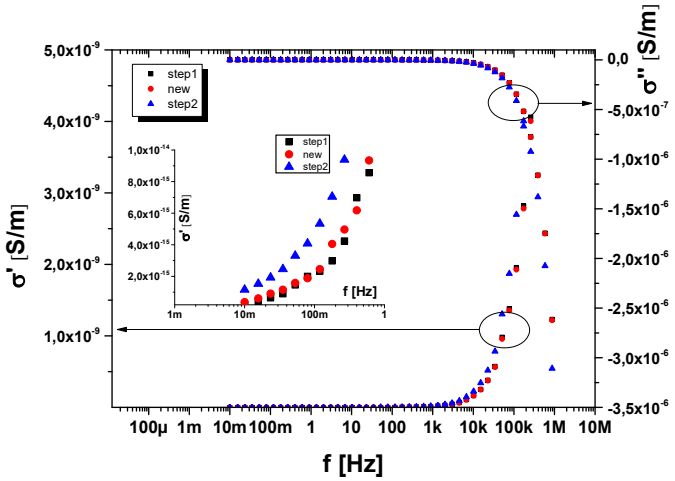

Fig. 13. Frequency spectrum of complex AC conductivity (step 1 – sample aged for 3000 hours, step 2 – sample aged for 6000 hours)

4. Conclusion

The comparative microscopic and Raman spectroscopy examination of the reference samples and aged samples from glass-epoxy core rods used in composite insulators showed no observable traces of degradation. Long term exposure to the influence of a DC voltage field in a direction parallel to the glass fibers caused neither any electrolysis in the material nor any deterioration of its electrical (electro insulation) or mechanical properties. The increasing polymerization of epoxy resin was the only phenomenon observed. This effect was expected, however, and was not surprising in the view of the research results reported in the literature. At the same time it does not cause any decrease in the operational properties of the glass-epoxy material. Dielectric spectroscopy offered another confirmation to the above results – as compared with the fresh samples, the aged samples showed no differences that could suggest any degradation processes.

REFERENCES

[1] J.M. George, Z. Lodi, Design and selection criteria for HVDC overhead transmission lines insulators, CIGRE Canada, Conference on Power Systems, Toronto, October 4-6, (2009).

[2] M. Kumosa, D. Armentrout, B. Burks, J. Hoffman, L. Kumosa, J. Middleton, P. Predecki, Polymer matrix composites in high voltage transmission line applications, Proc. of the 18th International Conference on Composite Materials, Jeju Island, S. Korea August 21-26, (2011).

[3] S. Gubański, Surface Charge & DC Flashover Performance of Composite Insulators, INMR August 13, (2016).

[4] P. Morshuis, A. Cavallini, D. Fabiani, G.C. Montanari, C. Azcarraga, Stress Conditions in HVDC Equipment and Routes to in Service Failure, IEEE Transactions on Dielectrics and Electrical Insulation **22**, No. 1, February (2015).

[5] CIGRE 518, Outdoor Insulation in Polluted Conditions: Guidelines for Selection and Dimensioning, Part 2: The DC case, Working Group C4. 303, December (2012).

[6] R.A. Ghunem, Li-Lin Tay, H. Terrab, A. H. El-Hag, Analysis of service-aged 200 kV and 400 kV silicone rubber insulation in the Gulf region, IEEE Electrical Insulation Magazine **23** (6), 3539-3546 (2016).

[7] RRUFF Data Base Department of Geosciences, University of Arizona, 1040 E 4th, Tucson, AZ, USA. 85721-0077.

[8] Filipecki, M. Sitarz, A. Kocela, K. Kotynia, P. Jelen, K. Filipecka, M. Gaweda, Studying functional properties of hydrogel and silicone-hydrogel contact lenses with PALS, MIR and Raman spectroscopy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **131**, 686-690 (2014).

[9] K. Filipecka, R. Miedziński, M. Sitarz, J. Filipecki, M. Makowska-Janusik „Optical and vibrational properties of phosphorylcholine-based contact lenses – Experimental and theoretical investigations, Spectrochimica Acta Part A **176**, 83-90, (2017)

[10] B. Grabowska, M. Sitarz, E. Olejnik, K. Kaczmarska, FT-IR and FT-Raman Studies of Cross-Linking Processes with Ca^{2+} Ions, Glutaraldehyde and Microwave Radiation For Polymer Composition of Poly(Acrylic Acid)/Sodium Salt of Carboxymethyl Starch – Part I, Spectrochimica Acta Part A **135**, 529-535 (2015).

[11] B. Grabowska, M. Sitarz, E. Olejnik, K. Kaczmarska, B. Tyliszczak, FT-IR and FT-Raman studies of cross-linking processes with Ca^{2+} ions, glutaraldehyde and microwave radiation for polymer composition of poly(acrylic acid)/sodium salt of carboxymethyl starch – In moulding sands, Part II, Spectrochimica Acta Part A **151**, 27-33 (2015).

[12] I. Plesa, P.V. Notingher, S. Schlögl, Ch. Sumereder, M. Muhr, Properties of Polymer Composites Used in High-Voltage Applications, Polymers **8** (5), 173 (2016).

[13] Jingkuan Duan, Jun Zhang, Pingkai Jiang, Effect of External Electric Field on Morphologies and Properties of the Cured Epoxy and Epoxy/Acrylate Systems, J. Appl. Polym. Sci. **125** 2, 902-914 (2012).

[14] G. Babich, G. Cherevashchenko, Modification of the Epoxy Resin by Use of Electric Field, 2011, https://www.pegasus-europe.org/Pegasus_AIAA/papers/ 2011_Babich_Kharkiv.pdf (2011).

[15] Y. Cheng, X. Zhao, M.G. Danikas, D.D. Christantoni, P. Zairis, A Study of the Behaviour of Water Droplets under the Influence of Uniform Electric Field in Epoxy Resin Samples, J. El. Eng. **63**, 3, 196-200 (2012).

[16] A. Krivda, S.A. Page, G. Meier, S. Wright, Dielectric Spectroscopy of Fiber-Reinforced Epoxy Materials, Proc. of the 2004 IEEE International Conference on Solid Dielectrics, Toulouse. France, July 5-9, (2004).