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Thermal and voltage treatments of silicone/mica high-temperature electrical insulation

Abstract. *The influence of thermal and voltage treatments on the properties and the inner structure of high-temperature composite based on mica and a silicone binder was analysed. Thermal treatment was simulated by an unrepeated thermal stress of 320 °C for a time of 500 hours. The material was also exposed to electric field intensities ranging from 9.6 to 15.9 kV/mm for times ranging from 7 to 280 hours. Dielectric characteristics, such as volume resistance, dissipation factor and relative permittivity were measured. Specimens were also analysed via Fourier Transform Infrared Spectroscopy and microscopic analysis. As measurements have proven, accelerated thermal treatment has no significant effect on the observed characteristics. On the contrary, voltage treatment causes very expressive degradation of the material, which comes out as marked deterioration of all of the observed properties.*

Streszczenie. *Przedstawiono wyniki badania wpływu zmian temperatury i napięcia na właściwości i strukturę kompozytów wysokotemperaturowych bazujących na mice i spoiwie krzemowym. Materiał badano przy zmianach temperatury oraz pola elektrycznego 9.6 do 15.9 kV/mm. Materiał badano też z wykorzystaniem spektroskopii widma podczerwonego. Szybkość zmian temperatury nie miała większego znaczenia natomiast zmiany napięcia powodowały degradację materiału. (**Badania wpływu temperatury i napięcia na wysokotemperaturowy kompozyt izolacyjny**)*

Keywords: composites; electrical insulation; aging; Fourier Transform Infrared Spectroscopy.
Słowa kluczowe: kompozyty izolacyjne, starzenie, wpływ temperatury

Introduction

Composites are essential parts of insulating systems of all electric equipment. Their fundamental purpose is to separate two areas with different electrical potentials, so the electric current cannot pass between them. Hence, electric equipment is unthinkable without correctly designed composite insulating materials. Besides the insulating function, there are many other requirements that these materials have to meet. Such requirements depend on the concrete application, electric equipment construction and, in particular, operating conditions. In the long term, composites are exposed to a combination of thermal, electrical and mechanical stresses during service operation. These stresses cause ageing, which can finally lead to insulation breakdown [1].

In a single machine, there is a wide spectrum of various composites, mainly composites with the polymers as their key components (see e.g., [2]). Large electrical machines used in the power industry (generators, power transformers, engines etc.) most often contain composites with permanent thermal resistances in the range from 90 to 180 °C. Considering the significance of these machines, great attention is paid to their testing [3, 4]. Other operation temperatures must be taken into account as well (in some cases composites designed for operation temperatures more than 250 °C have to be used). This material group includes special composite materials used at extreme temperatures, e.g., in nuclear reactors (to create the insulating system of linear step motors for fuel rod control) or in an induction furnace (to protect the electrical coils from mechanical stress). They are also used in common household appliances, such as microwave ovens. These so-called “high-temperature insulating materials” have completely different ageing processes and, in particular, different electrical properties than commonly used materials.

High-temperature insulating materials are most often made from inorganic materials [2]. The most widely used composites are those based on silicon/mica combinations, which provide excellent high temperature resistance [5], as well as good electrical properties. Although this material group is very interesting, sufficient attention has not been paid to it until now. Many authors focus mainly on silicone rubber [6-10], e.g., Sandén [6] deals with the testing of mixtures containing silicone rubber that could be used as thermal insulation in jet engines. He is satisfied that silicone-based insulations have much higher heat insulating capability than HTPB (hydroxyl-terminated polybutadiene) or materials based on epoxy resins. Additionally, Oldfield [7] published very interesting results about ageing of ten different silicone elastomers, which have been exposed to Australian hot-wet, hot-dry and temperate environments for 20 years. This study proved that specimens of most of the tested elastomers remained intact and uncracked. From the view of electrical properties, the study by Yong Zhu [8] should be mentioned. It demonstrates higher resistance of silicone rubber to corona discharge than insulation made from ethylenvinylacetate. Mica, with its excellent properties, is also a very common item in the literature [11-13]. Besides the exceptions ([14]), there is still very little information on ageing mechanisms of silicone/mica high-temperature insulations.

As is generally known, the silicone binder (mostly polydimethylsiloxane) undergoes the oxidative degradation to silica SiO_2, carbon dioxide CO_2 and water H_2O (unzipping reaction and random scission) above 350 °C. Very little smoke is evolved and carbon black is not formed during this thermal degradation. The remaining SiO_2 main chain joins the mica fillers and creates a structure of high mechanical strength. The thermal resistance of such ceramified product is limited by the resistance of the fillers and support materials [14-16].

In addition to the knowledge of chemical processes accompanying the ageing process of these materials, it is also necessary to focus on its performance in service, especially on the trend of their electrical characteristics, as these materials are very often used as electrical insulations. Therefore, one representative of such a group of materials is tested. The main objective is to describe the influence of the most common degradation factors (temperature and voltage stress) on the inner structure and electrical properties of the tested material.

Experimental

A. Material description

Composite designed for working in extreme operating conditions, under high temperature stress and electric field stress, was analysed. Material is composed of 91% noncalcinated mica (white mica) and 9% thermally resistant silicone binder (Wacker Chemie AG). The silicone binder used in this material contributes to the thermal resistance of the composite. The binder consists of pure polymethylsiloxane and contains 82% SiO_2 groups after full oxidation. This binder is also characterized by excellent binding forces to most of the inorganic materials and by thermal resistance up to 300 °C without any marked deterioration of electrical or mechanical properties. By compressing these components at high temperature and high pressure to the shape of compact hard boards, a material that conformed to the defined requirements, i.e., steady thermal resistance up to 500 °C, was produced.

B. Accelerated thermal and voltage treatment

Considering the common usage of the tested material, mainly thermal and voltage treatments were applied. Thermal treatment was simulated by an unrepeated thermal stress of 320 °C for a time of 500 hours. The voltage treatment followed (Fig. 1).

Fig.1. Voltage treatment of specimens

For this purpose, special brass electrodes (115×115 mm in size, thickness of 5 mm, corner radius of 10 mm and chamfer of 2.5 mm) were made. Table 1 shows an overview of the voltage levels and the times of accelerated voltage treatment.

The voltages and times were chosen at the very first orientation short-time tests of dielectric breakdown voltage. Measurements were first performed with untreated specimens (in virgin state), then with thermally treated specimens and finally in single times of accelerated voltage treatment according to Table 1.

Table 1. Overview of voltage levels and times of accelerated voltage treatment

Voltage U_{exp} [kV]	El. field intensity E [kV/mm]	Exposure time t_{exp} [hours]
3	9.6	80, 140, 200, 280
4	12.8	20, 50, 80
5	15.9	7, 14

C. Specimens preparation and methods description

The tested material was provided by a manufacturer in the form of hard boards, 200×200 mm in size and with an average thickness of 0.3 mm. The square-shaped specimens, 100×100 mm in size, were cut from the boards. Electrical characteristics (volume resistance, dissipation factor and relative permittivity) were first measured on prepared specimens; these specimens were then analysed via Fourier Transform Infrared Spectroscopy in combination with the Technique of Attenuated Total Reflectance (FT-IR ATR) and, also, by microscopic analysis.

Volume resistance

Volume resistance R_x [Ω] was measured with an electrometer with an internal source of DC voltage (Keithley Instruments, model 6517) and a three-electrode system (Keithley Instruments, model 8009). Measurements proceeded in accordance with the IEC 60093:1980 Standard [17] and under a DC voltage of 500 V. Steady state current was recorded after 100 minutes of polarization.

Dissipation factor and relative permittivity

Measurements of dissipation factor and relative permittivity were performed on a VKB BN 3520 Schering Bridge (Rohde&Schwarz). Measurements proceeded according to the IEC 60250:1969 Standard [18]. The dissipation factor and the relative permittivity were measured at the commercial power frequency of 50 Hz and voltage of 30 V.

Measurement frequency of volume resistance, dissipation factor and relative permittivity was 10; obtained values were, consequently, averaged.

FT-IR ATR

The technique of Attenuated Total Reflectance was used during the FT-IR measurement. The technique is based on the principle of multiple total reflection of radiation on the sample-crystal interface [19-21]. Infrared spectra from the surface of the tested specimens were collected on a Nicolet 380 FT-IR spectrometer with a Smart MIRacle ATR cell (ZnSe crystal). Due to the high inhomogeneity of the tested material, specimens were measured with a minimum frequency of 20, whereas 32 scans with a resolution of 4 cm^{-1} were collected and averaged for each of these measurements. OMNIC software and TQ Analyst Professional Edition were used (after the automatic correction of base line) for the display and analysis of the collected spectra.

Microscopic analysis

Microscopic analysis was performed via Olympus LEXT OLS 3000 confocal laser microscope. Structural changes were examined on the specimen surface, as well as on the cross section. During the cross section preparation, the specimen was stabilized in a two-component acrylate resin (with ceramic filler for strengthening of the whole structure).

Results and discussion

It is necessary to note, that the first two points in Figs. 2–4 are shared between all of the obtained curves. These points correspond to virgin specimens and specimens after the thermal treatment of 320 °C for 500 hours (the time axis is not on a logarithmic scale for these two points by reason of lucidity of the graphs).

A. Volume resistance

Results of the volume resistance measurement are presented in Fig. 2. As results showed, volume resistance of all the treated specimens was markedly decreasing compared to the virgin specimens in reaction to the applied treatment, and the thermal treatment had a much lesser effect on the specimens than the voltage treatment. Fig. 2 also illustrates that a treatment of higher voltage applied over a shorter period of time caused more expressive degradation than a lower voltage treatment over a longer time interval.

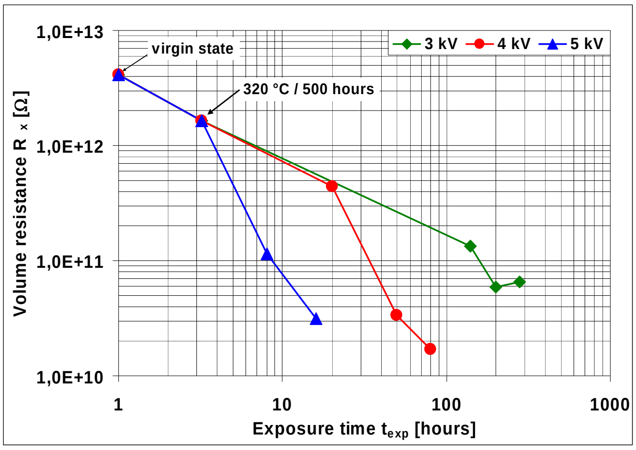

Fig. 2 Volume resistance dependence on the duration of the thermal and voltage treatment

B. Dissipation factor and relative permittivity

Figure 3 presents the results for the dissipation factor, expressing the dielectric losses during the polarization processes caused by applied voltage. In particular, the influence of the voltage treatment intensity is evident from the curves.

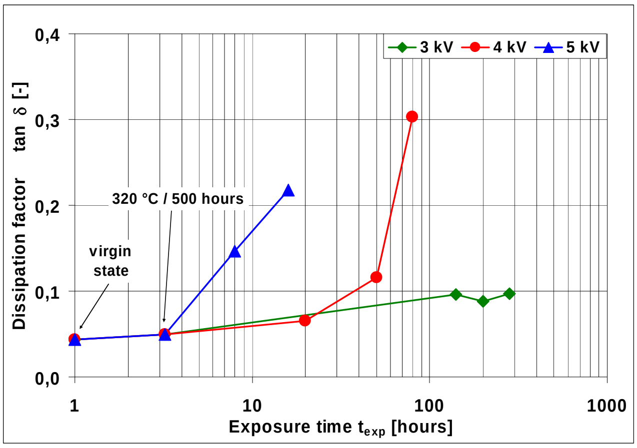

Fig. 3 Dissipation factor dependence on the duration of the thermal and voltage treatment

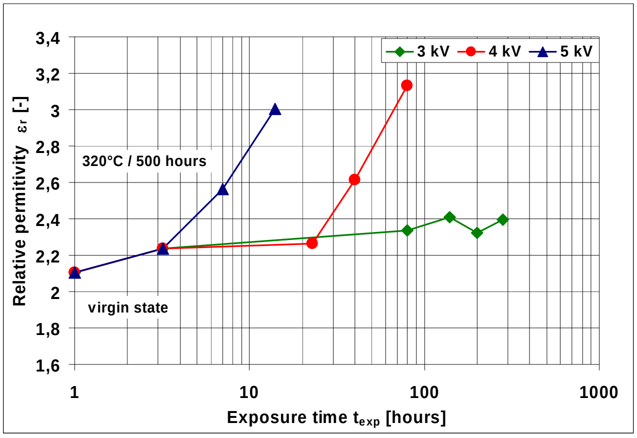

Fig. 4 Relative permittivity dependence on the duration of the thermal and voltage treatment

The first two points of the curves show that the thermal treatment had no expressive effect on the value of the dissipation factor, which is in accordance with the volume resistance measurements. As we look at the following points of the curve that correspond to the single voltage treatment levels, we can observe that a voltage treatment of 3 kV causes only a slight increase of the dissipation factor. The other voltage levels (4 and 5 kV) cause very significant increases; thus, it is possible to expect the irreversible changes in material. This effect is documented very well, mainly at a voltage level of 4 kV, where just a slight increase of the dissipation factor is observed after the first two times (20 and 50 hours) of treatment; the voltage treatment of 80 hours causes a very significant increase of these characteristics.

Irreversible changes of the material electrical properties are proven also by relative permittivity measurements (see Fig. 4). Relative permittivity increases dramatically in reaction to the thermal and voltage treatment, as evident from Fig. 4. These high values point to an increasing tendency of the material to store the electric charge in its inner structure, which causes dielectric losses.

C. FT-IR ATR

As noted previously, material was analysed also by FT-IR spectroscopy, using the ATR technique. Figure 5 shows the infrared spectra of two components of this material separately (white mica and silicone binder) as well as the spectra of the whole composite in the virgin state. Figure 5 illustrates a result typical for IR analysis of composite materials, i.e., the spectra of white mica and the silicone binder interact with each other, which worsens the interpretation of the final spectrum of whole composite.

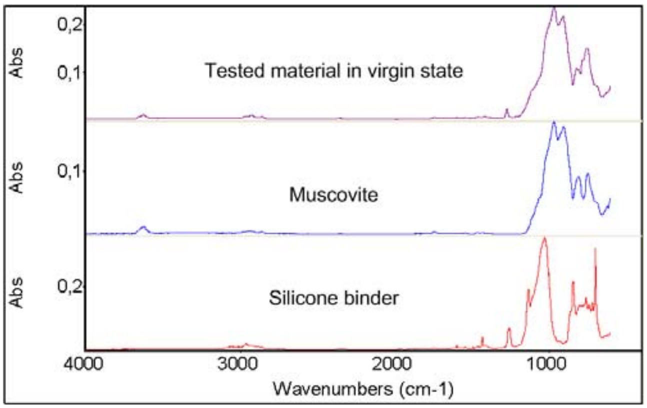

Fig. 5 Infrared spectra of tested material and its components (white mica and silicone binder)

When the response of such a material to several related factors (e.g., thermal and voltage treatment) is examined, it is convenient to use the method of so-called “multidimensional sampling” for spectral processing [22]. The principal component analysis (PCA) seems to be a suitable method for the analysis of this sampling. The principle of PCA consists of the replacement of the original variables (obtained spectra) by so-called principal components (PC). Data dimensionality decreases in this manner, as only a certain number of principal components is selected in place of the original variables. These components represent the main spectral variation [23-25].

The aforementioned method was applied in our case. TQ Analyst Professional Edition software was used for the assessment of spectral variation when six principal components have been specified. For full spectral interpretation, only the first three principal components were involved because they explain 99,462% of the total variance of the source spectral matrix (they represent the main portion of the variation in spectra). PC1 (91,194%), PC2 (7,731%) and PC3 (0,538%) as the most significant components are presented in Fig. 6 (negative bands were removed from these spectra).

PC1 corresponds to the variability of the material organic matrix, which is based on aliphatic hydrocarbons

(3000 – 2800 cm^{-1} region), and it also contains the carbonyl group (carbonyl stretching vibration 1700 cm^{-1}). The second principal component (PC2) corresponds to the variability in the spectral response of white mica and the third one (PC3) corresponds to the silicone variability.

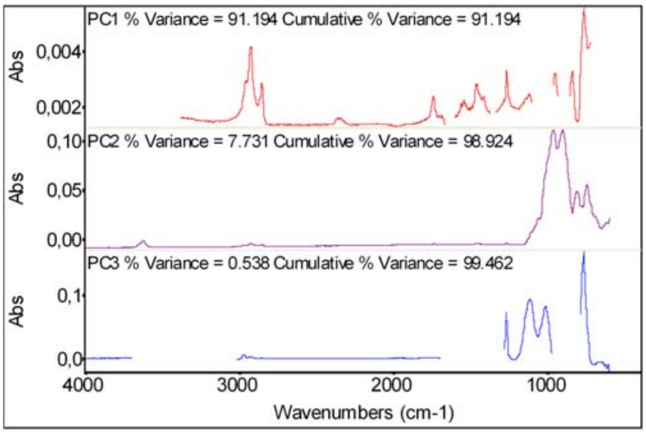

Fig. 6 Spectra of principal components

During the spectral analysis within the applied treatment, it is important to pay attention to those spectral bands, which were included in principal component spectra. The most significant changes are observed in the 1700 – 1200 cm^{-1} region (see Fig. 7-9) and the 3000 – 2800 cm^{-1} region (see Figs. 10-12); these regions occur mainly in the silicone binder spectrum (see spectrum of the binder in Fig. 5 and the PC3 spectrum in Fig. 6). Figures 7-9 illustrate very obvious trends in the obtained spectra that fully correspond to the results of electrical property measurements.

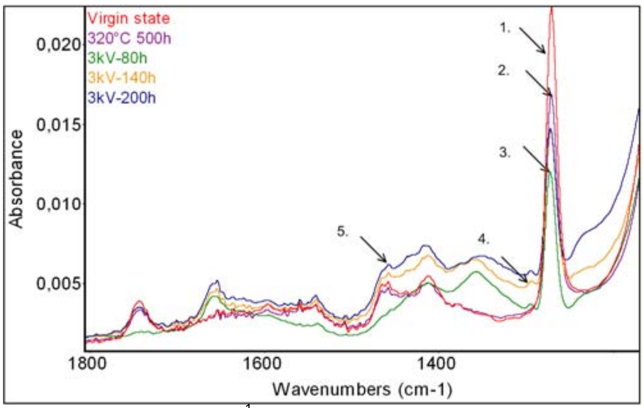

Fig. 7 1700 – 1200 cm^{-1} – comparison of spectra (thermal and voltage treatment at 3 kV)

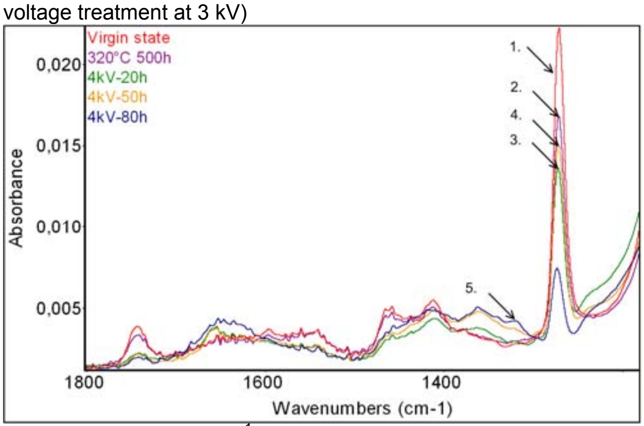

Fig. 8 1700 – 1200 cm^{-1} – comparison of spectra (thermal and voltage treatment at 4 kV)

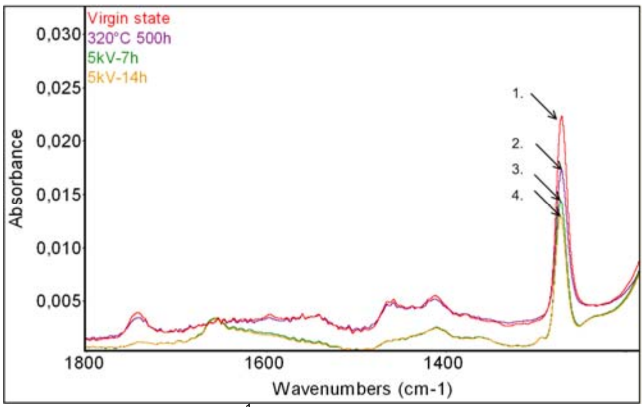

Fig. 9 1700 – 1200 cm^{-1} – comparison of spectra (thermal and voltage treatment at 5 kV)

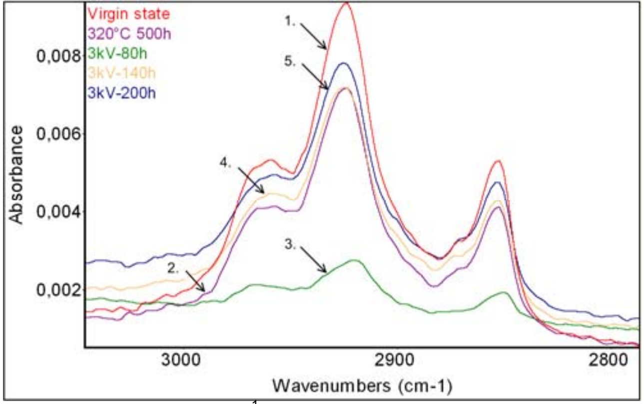

Fig. 10 3000 – 2800 cm^{-1} – comparison of spectra (thermal and voltage treatment at 3 kV)

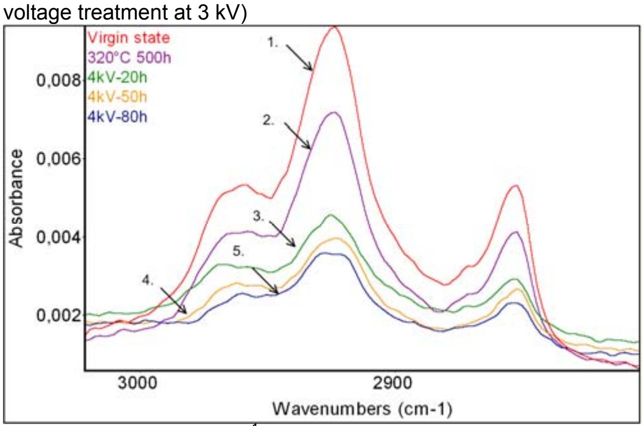

Fig. 11 3000 – 2800 cm^{-1} – comparison of spectra (thermal and voltage treatment at 4 kV)

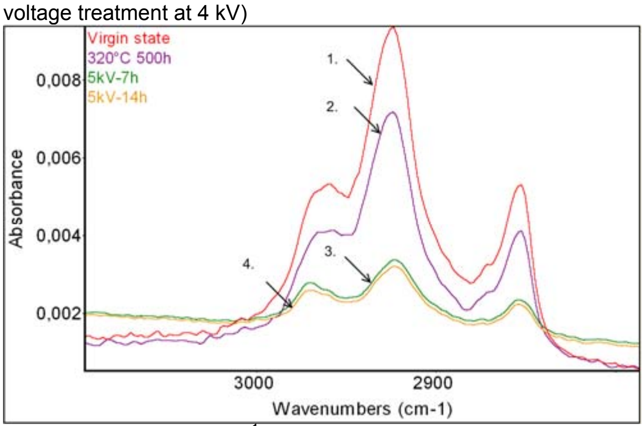

Fig. 12 3000 – 2800 cm^{-1} – comparison of spectra (thermal and voltage treatment at 5 kV)

As evident, the intensity of spectral bands increases rapidly due to thermal and voltage treatment in the 1700 – 1200 cm^{-1} region. It is also evident that the obtained spectral bands of the virgin material and the thermally treated material almost overlap, which refers to smaller influence of the thermal treatment compared to the voltage one. All spectra have the expressive tendency to decrease mainly in the cases of 4 kV and 5 kV levels of voltage treatment, while no such expressive trend was observed at the voltage level of 3 kV. The graphs representing the 3000 – 2800 cm^{-1} region (aliphatic hydrocarbons) in Figs. 10-12 also support these conclusions.

D. Microscopic analysis

The microscopic analysis helped to analyse the structure of the surface and cross section of specimens. The specimens in the virgin state, after the thermal treatment and also after the greatest voltage treatment (5 kV/14 hours) were tested. Figure 13a (virgin material) presents the layer morphology typical for mica-based materials. Boundaries of the single mica particles are clearly evident in comparison with the silicone binder, which is hardly recognizable in this scan. As we compare the virgin material to the thermally treated material (Fig. 13b), we can see that no significant changes in the structure were recorded by the microscopic analysis.

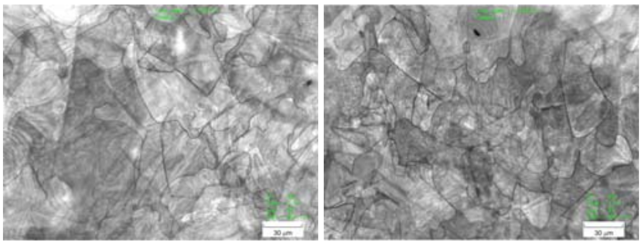
a) b)

Fig. 13 Microscopic analysis of the specimen surface: a) virgin material, b) material after 500 hours of thermal treatment of 320 °C

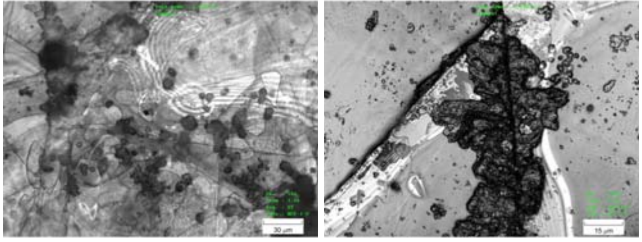
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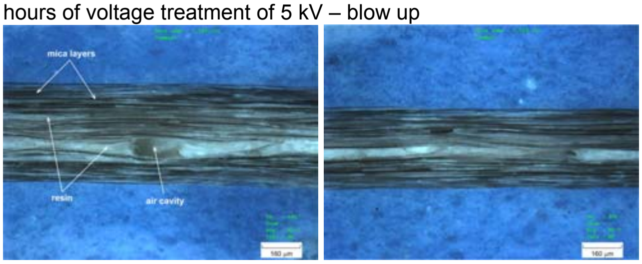
Fig. 14 Microscopic analysis of the specimen surface: a) material after 14 hours of voltage treatment of 5 kV, b) material after 14 hours of voltage treatment of 5 kV – blow up



a) b)

Fig. 15 Microscopic analysis of the specimen cross section: a) virgin material, b) material after 500 hours of thermal treatment of 320 °C

On the contrary, an electric field of high intensity causes very expressive changes in specimen morphology, as is obvious in Fig. 14. Its application leads to the decomposition of the organic matrix of the binder and to the creation of regions of degradation.

These regions (microscopic cavities) are considered to be very dangerous from the point of view of composite performance in service because they are the points where so-called partial discharges could originate and accelerate, thus initiating the degradation process of the insulating material (they could cause short-circuit very easily) [26-29].

These conclusions are also proven by the scans of the specimen cross section (see Figs. 15 and 16), where the high inhomogeneity of material is evident.

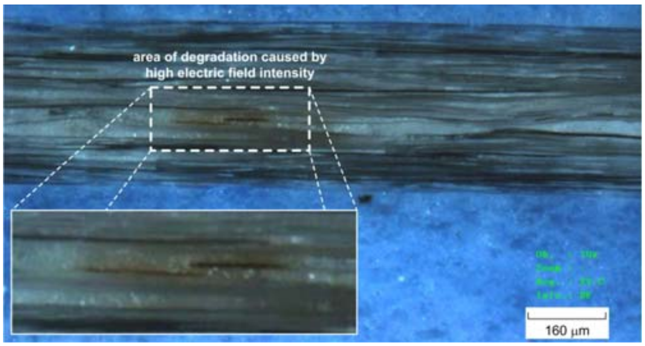


Fig. 16 Microscopic analysis of the specimen cross section after 14 hours of voltage treatment of 5 kV

Conclusion

This paper deals with the study of the influence of applied thermal and voltage treatment on the electrical and structural properties of composite material based on mica and silicone binder. Dissipation factor, volume resistance and relative permittivity were measured, since the electrical insulating material was tested. The measurements did not show a very significant influence of even intensive thermal treatment (320 °C / 500 hours) on these characteristics. On the contrary, marked influence of the voltage treatment on the degradation of this material was observed. An electric field of high intensity causes partial discharges inside the inner structure of the material. As microscopic analysis proved, these discharges are, consequently, the reason of very destructive changes in the material structure. Degradation caused by the voltage treatment expressed itself as rapid deterioration of all of the monitored electrical properties; while the dissipation factor and relative permittivity increased, volume resistance decreased rapidly. The resultant electrical characteristics reached an unacceptable level from an operational point of view.

Infrared spectroscopy also definitely confirmed the negative changes in the tested material structure. Considering the inhomogeneity of the tested material, the application of principal component analysis (PCA) was necessary for a proper interpretation of the obtained spectra. PCA proved that 91.2% of all changes occur in the organic matrix of material. The lower intensity of bands in the spectra refers to the degradation of the organic groups of polymethylsiloxane (changes of spectra of aliphatic hydrocarbons and carbonyl groups).

Measurements also pointed to a good correlation between electrical tests and FT-IR ATR results. It can be stated in conclusion that the tested material has very good thermal resistance but, in operation, it is necessary to monitor the influence of the electric field, which can be very destructive at high intensity levels.

Acknowledgements

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