OPTIMALIZATION OF THE THERMAL CURING OF EPOXY BASED INSULATIONS

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ABSTRACT

There is difficult to imagine modern production of electrical devices without components containing organic substances. This fact is mainly concerned to composite materials, in which the bond component is made of organic substance. The intricate curing reactions have been proceeding during the composites technological curing as well as during the device operation, where mostly the thermal-oxidative reactions, leading to material degradation, occur. For above-mentioned reasons, there is given big attention to the study of the reactions proceeding in the material.

Monitoring of the properties and applicability of high-voltage insulating systems containing epoxy resins require knowledge of curing degree of these resins. This curing degree is considered to be the key parameter for quality of materials used for these systems. Application of Differential Thermal Analysis (DTA) for evaluation of curing degree of three-component composite materials (glass fabric, reconstructed mica, epoxy resin) is presented in the article. Used analysis enables to observe characteristic structural parameter – the concentration of reactive particles in organic component of this material. In our investigation, concept of curing reactions courses was obtained as well as the details for determination of optimal curing time of material. These conclusions have been confronted with the other methods such as Thermomechanical Analysis (TMA) or dissipation factor and complex permitivity determination. Based upon these results it is obvious, that the conclusions correspond to one another.

Electrical properties of high voltage-high temperature insulation materials depend on the curing degree of the used resin. The new modified high temperature resistant epoxy resins were used in the three-component composite materials. The main objective of the investigation was to obtain the material with the best electrical properties.

Keywords: *composite insulation, permittivity measurement, dissipation factor, curing characteristic, dielectric polarization.*

1. INTRODUCTION

The insulating system is the main, inseparable part of electrical rotating machines. High operating and reliability demands require the proper technological steps to manufacture the insulating system.

Electrical properties of the insulation such as dissipation factor and permittivity are dependent on curing temperature. The curing process of electro-insulating materials is one of the mentioned technological steps necessary for three-component composite manufacturing. The crosslinking of bond resin occurs, and the insulating system obtains its final properties during this curing process.

It is useful to know the curing degree of composites materials for high-voltage application (Resin-rich in our case) at a given temperature and curing time. Resin-rich technology is the most used technology to manufacture the insulation of the high voltage rotating machines. The impregnated tape is used to create the machine insulation. The tape contains a carrier, filler and bond. A carrier is mainly fiber glass, Polyethylene (PE) or Polyethylene terephthalate (PET). The mica or re-mica paper is used as filler in the high voltage machines. Mica is employed in high voltage composites for its high electric breakdown voltage as a dielectric barrier. The bond content in the tape is approximately 40%. Modified epoxy resin serves as a bond usually.

The investigation of the optimal curing time and temperature of new developed insulating materials (containing glass fabric, epoxy resin and mica) is the main objective of this paper. The results allow to obtain the best final electrical properties of cured material.

The structural analysis, Differential Thermal Analysis (DTA) and Thermo-Mechanical Analysis (TMA), combined with measuring of the Dissipation factor (tan δ) curing characteristics helps to determine optimal curing conditions, e.g. [15]. The study of tan δ curing characteristics makes possible to determine the optimal curing temperature (tan δ curing characteristics is the tan δ dependence on curing time) [8], and suitably applied structural analysis determines the optimal curing time when the resin is fully crosslinked.

2. USED ANALYSIS

DTA is the first structural analysis applied to evaluate the insulation. The physical principle of DTA is ca be explained by the equation (1). The activation energy E which reflects the level of reaction-able particles in the material is critical important factor.

$$d(\Delta T) / dt + A\,(\Delta T - \Delta T_{stab}) = \\ = E / C_v \,.\, (dm_r / dt) \qquad (1)$$

where: ΔT is the difference in momentary temperatures of the sample and the inert standard,

ΔT_{stab} is the difference in temperatures indicated by the differential thermocouple – when the change of enthalpy in the sample doesn't occur – it corresponds to the zero line of the thermogram,

A (s^{-1}) is the preexponential factor determining the frequency of molecule collision [8],

E ($J.mol^{-1}$) is the activation energy, which represents the reaction capability of particles in material,

C_v ($J.kg^{-1}.K^{-1}$) is the thermal capacity of the sample and the container of DTA cell,

mr (%) is the relative concentration of active particles:

$$m_r = (m_0 - m) / m_0 \quad (2)$$

where: m_0 is the number of molecules entering the monitored reaction, and m is the number of particles, which is fixed during the reaction.

DTA analysis based on this physical principle is suitable for the observation of the curing degree of insulating systems containing organic resins.

TMA is studying the displacement of the tested material depending on the linearly changed temperature. At the same time the mechanical stress is applied. The output of this analysis is the determination of the Glass Transition Temperature T_g (˚C) and the Thermal Expansion Coefficient α (ppmºC^{-1}).

$$\alpha_P = \frac{1}{\Delta t} \cdot \frac{\Delta h}{h} \quad (3)$$

where: αP is average thermal expansion coefficient,
Δt test temperature interval,
Δh sample dimension gain,
h (μm) starting sample dimension.

$$\alpha_L = \frac{dh}{dT} \cdot \frac{1}{h} = \frac{dh}{dt} \cdot \frac{1}{\beta_n \cdot h} \quad (4)$$

where αL is local thermal expansion coefficient,
β_n rate of temperature rise,
T (K) temperature.

The T_g is structural parameter that describes the material structure. The material changes its properties (from glassy to rubbery phase) at the temperature T_g. To know this parameter is crucial, and TMA analysis (used for T_g determination) also takes an important place in diagnostic system of the described project.

3. DIELECTRIC PROPERTIES

The dielectric properties of a material during a curing are primarily affected by the polarization and conduction mechanisms.

The complex permittivity ε^* and its real ε' and an imaginary ε'' (loss factor) part were chosen as parameters of the investigation. The real part of ε* is equal to the relative permittivity of the dielectric material. The loss factor ε'' is proportional to the losses, and it is equal to the energy losses due to dipole movement under an AC electrical field. The equation (5) gives the loss factor:

$$\varepsilon'' = \varepsilon''_{ion} + \varepsilon''_{dipol} \quad (5)$$

ε''_{ion} is the part relative to the ion conductivity, and ε''_{dipol} is the part relative to the dipole relaxation polarization.

The subscript "ion" indicates the contribution of the ionic conductivity whereas the subscript "dipole" indicates the contribution of dipolar relaxation to the loss factor ε''.

The part ε''_{ion} is given as:

$$\varepsilon''_{ion} = \sigma / 2\pi f \varepsilon_0 \quad (6)$$

where: σ (S) is the ionic conductivity, f (Hz) is the applied frequency and ε_0 is the dielectric constant of vacuum.

At the beginning of the curing reaction (low degree of cure), the contribution of the ionic conductivity is dominant, and the value of relative permittivity ε' is high. As the curing reactions precedes further, the epoxy crosslinking and dipole relaxation become more dominant. This can be monitored as a peak in the dielectric dissipation factor curve.

The Havriliak-Negami function [4] is used to describe the behavior of complex permittivity, loss factor and dipolar contribution respectively.

$$\varepsilon^* = \varepsilon_\infty + \varepsilon_0 - \varepsilon_\infty / \left[1 + (j\omega\tau)^\alpha\right]^\beta \quad (7)$$

where τ (s) is the relaxation time, ω (s^{-1}) is the applied frequency, ε_0 is the relaxed or static dielectric permitivity, ε_∞ is the unrelaxed permitivity, α and β are parameters between 0 and 1, ζ is a parameter, j is an imaginary unit. The exponent α describes the interval of the distribution of relaxation times while the exponent β describes the skewness of the distribution of relaxation times.

For the loss factor tan δ and loss number ε'' determination, the Debye theory [1] is used. The parameters ε' and ε'' are consequently given as:

$$\varepsilon' = C_x / C_0 \quad (8)$$

where: C_x (F) is the measured capacity with actual dielectric, C_0 (F) is the capacity with vacuum determined according to IEC 250 standard. The loss number ε'' is determined according to Debye theory [1] as:

$$\varepsilon'' = \varepsilon' \cdot \tan\delta \quad (9)$$

4. SAMPLES SETUP

The Insulation material samples for curing tests were prepared using the standard shape taped materials for the Resin-rich method. The Resin-rich method is using controlled heat and pressure for material curing. Therefore the method is more suitable for curing of the insulation of big machines, than other technology used – Vacuum Pressure Impregnation (VPI). The later method utilize the vacuum chamber. Therefore it is usually not suitable practice for big machines manufacturing. The preparation of the test samples is shown in Fig. 1. The samples were cured in the three-electrode system Tettex 2914 YY. This system allows the control of the electrode temperature and the pressure applied on sample. This system was used both for the measurement of the dependence of the dissipation factor on the temperature (40˚C - 180˚C) and for the curing by constant temperature. Samples were

prepared using 50% overlap method. W is a tape width, Fig. 1. The prepared sample was placed into the electrode system. This system was preheated to the test temperature. On-line monitoring started two minutes after the sample insertion.

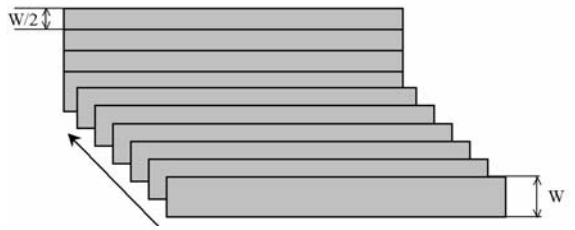


Fig. 1 The preparation of insulation material sample for curing test. W – the insulating tape width.

5. EXPERIMENT

The experiment concerning the curing of two different Resin-rich materials was designed because of new material development and its application necessity. The curing of a flat specimens was performed under six different isothermal temperatures. The temperatures were in the range of 130-180 °C.

The mica-glass composites are usually used as the main wall insulation of rotating machines containing mica paper, epoxy resin and glass fiber. The particular variants of the composites A and B (used in the experiment) differ from one another in the type of used epoxy resin curing agent. The dissipation factor dependence on the curing time was captured. The curing temperature was the parameter (130º - 180ºC). This dependence is called the Curing characteristic. The second examined was the tan δ temperature dependence. The measurement were performed on specimens cured for 200 min (on curing temperatures described above).

The temperature was increased from 40°C to 180°C in 1°C steps.

An experiment for a monitoring of the dielectric properties of electro-insulating materials during isothermal curing was proposed. This experiment consists of the curing analysis characteristics at six different curing temperatures within the range of 130 – 180 °C. The main objective was to observe the changes in the curing degree. It has been found that the properties depend on curing time, and the curing temperature.

The new materials were a new type of widely used mica composites.

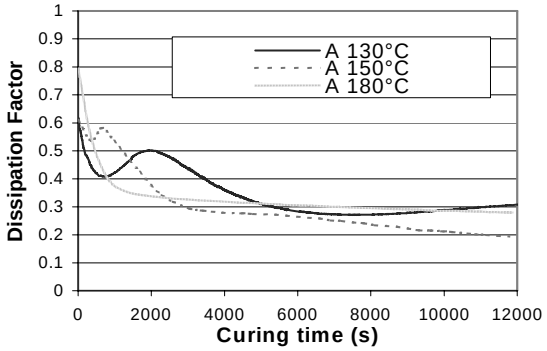
The particular variants of composites A and B differ from each other in the type of curing agent used. Exact formula of new advanced types of curing agent is proprietary.

6. RESULTS AND DISCUSSION

The results of the experiment described above are presented in Table 1. The minimum of material final dissipation factor was observed by curing at 150ºC.

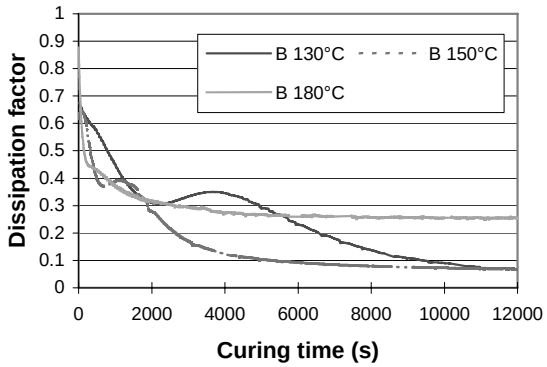
Table 1 Values of the dissipation factor depending on curing temperature after 200 min of curing.

Curing temperature (°C)	Dissipation factor Material A	Dissipation factor Material B
130	0.309	0.065
140	0.278	0.064
150	**0.193**	**0.063**
160	0.279	0.101
170	0.253	0.140
180	0.279	0.254



Graph 1 Dissipation factor dependence on curing time. Material A.

Graphs 1 and 2 present the example of the characteristics of tan δ dependent on the curing time. The peak of tan δ (given by dipolar relaxation [7]) depends on curing temperature - the higher the curing temperature, the earlier the peak appears (due to faster curing at higher temperatures).



Graph 2 Dissipation factor dependence on curing time. Material B.

At low curing temperatures material B does not show an increased final dissipation factor, unlike material A which shows a strong upward trend, however at high temperatures (>160°C) both materials show increased dissipation factors. This fact can be explained theoretically by two hypotheses. First, the delamination of the composite due to high temperature, and consequently the beginning of micro-inhomogeneities leads to increase of dissipation factor. The second hypothesis is that the rise of tan δ is due to increased number of polar particles due

to isomerisation processes inside the material structure [8].

The optimal curing temperature 150°C is estimated from the curing characteristic. The tan δ magnitude of the cured material reaches the lowest value at this curing temperature.

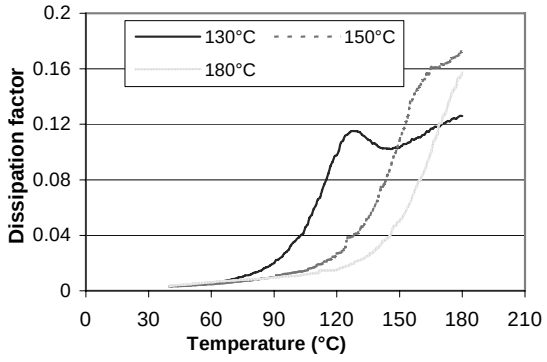
The measurement of tan δ temperature dependence (at materials cured for 200 min) was performed for verification of these results.

Experimental data from this test are shown in graphs 3 and 4. The imperfect curing of material A is evident at curing temperatures 130°C and 140°C. The decreasing of the tan δ comes into effect at the temperatures near the curing temperature. This occurs because of further curing of the epoxy resin. The study of relationships between curing char acteristics and tan δ temperature dependences confirms the most suitable curing temperature to be 150°C. The optimal electrical properties are evident from the presented graphs. The analysis of the curing characteristics (Table 1) yields of the optimal curing temperature of 150 °C, when tan δ of the cured system is reaching the lowest values.

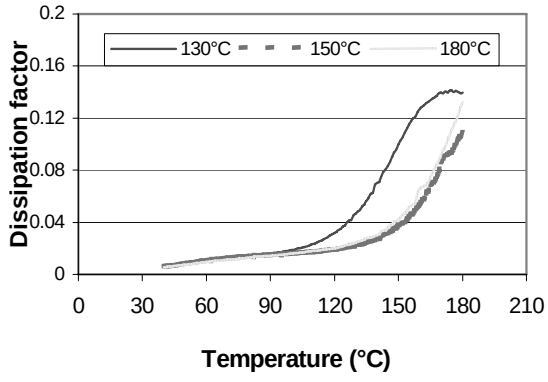
The DTA thermograms were measured with a temperature increase of 5°C/min up to max. 330°C. Graphs 5 and 6 present the material DTA thermograms. The thermograms contain two peak areas. The first peak area corresponds to the ratio of uncured particles, and it is the focused area.

The area of a second peak corresponds to the thermo-oxidative reactions. This magnitude is not so important for the curing degree evaluation.

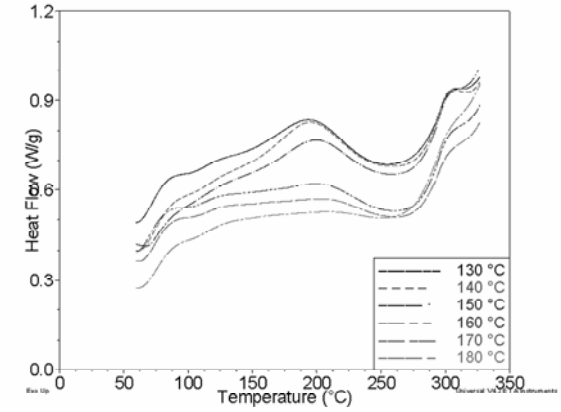
The DTA characteristic determined whether or not the material is fully cured or not.



Graph 3 Temperature dependence of tan δ of material A.



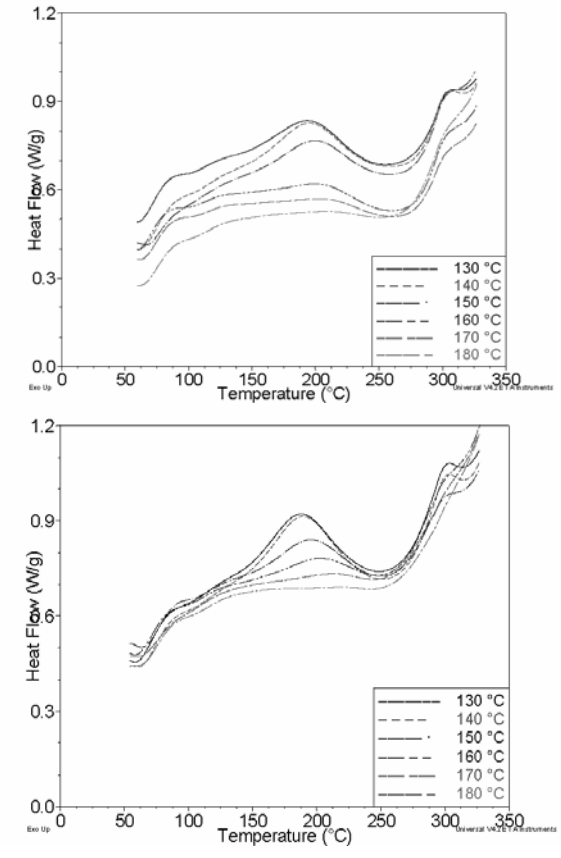
Graph 4 Temperature dependence of tan δ of material B.



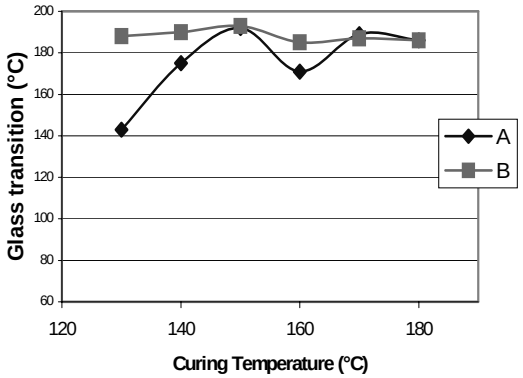
Graph 5 Results of the Differential Thermal Analysis of material A.

Graph 7 shows the results of the TMA analysis. The dependence of the glass transition, T_g on curing temperature have maximum at the curing temperature, of 150 °C. With the increase of the curing temperature, better crosslinking of the resin occurs. The higher T_g proves this phenomenon. At higher temperatures the material is overcured. During the process of curing, the high temperature ages cured material. That is the reason of the decrease of the T_g dependence at the temperatures higher then 150 °C, graph. 8. This result is in agreement with the dissipation factor dependences showed in graphs 1 and 2.

Graphs 8 and 9 show results of the real and imaginary part of the complex permittivity evaluation. When material is under cured, the permittivity is higher (130, 140 °C).



Graph 6 Results of the Differential Thermal Analysis of material B.



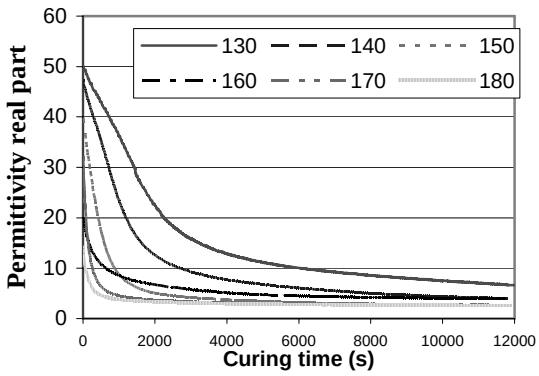
Graph 7 Glass transitions dependence of material A and B obtained from the Thermo-Mechanical Analysis.

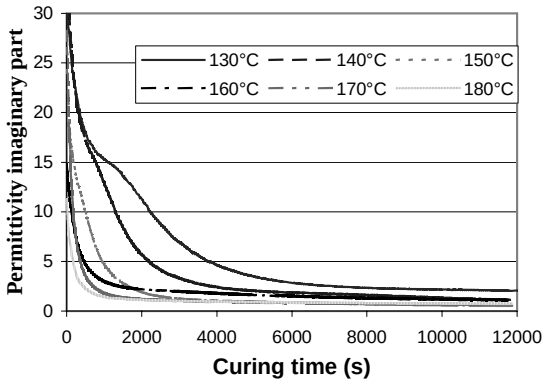
7. CONCLUSION

This paper has discussed the differences in behavior of two composite materials during the curing, and has shown a method of determining the optimal curing temperature in order to minimize the dielectric loss of the cured system.

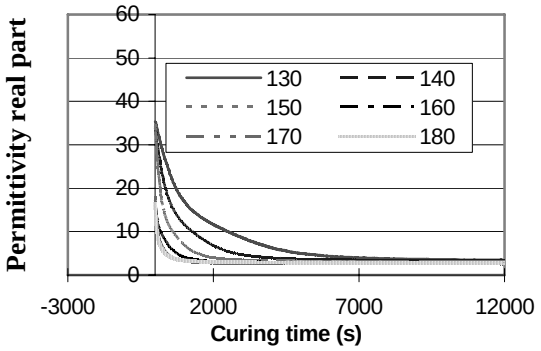
A detailed investigation shows the behavior of the dielectric properties during the curing of epoxy/mica/glass composite systems. The optimal curing temperature of the current materials appears to be 150 °C. It is suitable to use any structural analysis (for example DTA) for the determination of the optimal curing time [9]. The DTA test method, which follows the rate of reaction-able particles within material, allows to determine the moment of fully cured resin [8]. The optimal time of curing appears to be 3.3 h. The experiments enable an observation of the material from the view of chosen electrical and structural parameters, and study parameter changes with regard to applied curing temperature and curing time. The tan δ characteristics and theirs agreement with the results obtained from DTA and TMA give the answer for the optimal curing time and curing temperature of the insulating system.

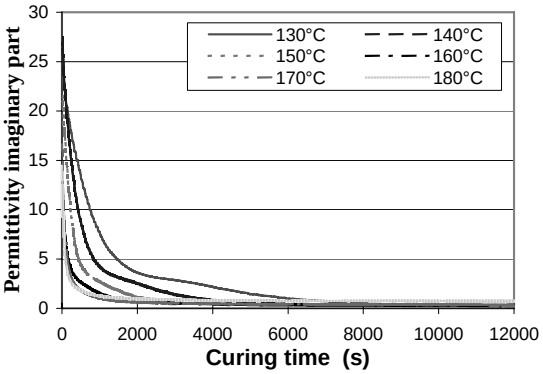
This method of observing the ratio of reaction-able particles is able to determine the point at which the insulating system is fully cured as well.





Graph 8 The real and relative part of the complex permittivity of material A.





Graph 9 The real and imaginary part of the complex permittivity of material B.

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Josef Pihera (IEEE Member since 2007) was born in Susice, Czechoslovakia in 1978. He received his Master degree in electrical engineering from University of West Bohemia, Plzen, Czech Republic in 2002 and his Ph.D. degree from the same university in 2005. He was student of University of Applied Science, Fachhochschule, Regensburg, Germany for six months and worked at the Department of High Voltage. He is an employee of the Department of Technologies and Measurement of the University of West Bohemia, Plzen. His research interests include dielectric spectroscopy of insulating materials, partial discharge and aging of electrical insulations.

Vaclav Mentlik was born in Plzen, Czechoslovakia in 1939. He published his doctoral thesis “Thermal analysis in diagnostics of high-temperature insulating materials” in the year 1985 in Faculty of Electrical Engineering at the Czech Technical University in Prague. He was promoted an Associate and later a Full Professor at University of West Bohemia in Plzen. He has been leading the Section of Electrical Technology in Faculty of Electrical Engineering at the same university since 1991. He leads the research team, which solved many research projects dealing with development and testing of electrical materials. He is the main leader of research project of Ministry of Education, Youth and Sports of Czech Republic, MSM 4977751310 - Diagnostic of Interactive Processes in Electrical Engineering (2005 – 2010). His main research interests include physics of electrical insulation materials; study of polarization phenomena in inhomogeneous dielectrics; operating conditions and environment; development and testing of a new electrical insulating materials and systems for application in electronics; application of structural analysis for testing of electrical insulating materials; diagnostics of electrical machines.