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The dielectric spectroscopy of epoxy resin with nanoparticles

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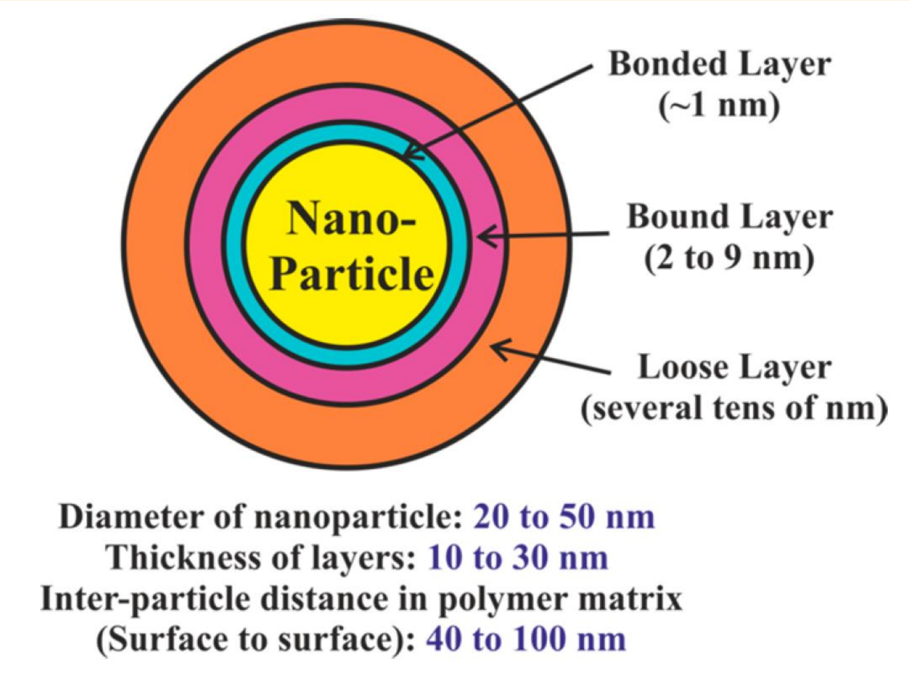
Interest areas of research:

- Dielectric spectroscopy of polyurethanes dopped by nanoparticles,
- The study of properties and changes in structural arrangement of nanoparticles in magnetic fluid,
- Investigation of structural changes of doped liquid crystals,
- The study of the phosphate glasses,
- Few years back the study of MOS structure by DLTS.

Introduction

- Polyurethane, polyethylene and epoxy resins ⇨ insulation materials used in electrical equipment, medium voltage cables, compound transformers . . .
- At use of insulating materials in electrical equipment for safe and reliable operation ⇨ the great dielectric and thermo- mechanical properties of insulation;
- These role polymers they took over, due to their unique characteristics and 70% of all produced polymers represent thermosetting resins and thermoplastics;
- The term “epoxy resin” refers to both the prepolymer and its cured resin/hardener system;
- Epoxy resins are widely used in various parts of the industry ... ⇨ they have excellent electrical insulation properties, so they are widely used as electrical insulating material;
- Insulation with defects (impurity, small gaps, bubbles, voids . . .) ⇨ a non-uniform distribution of the electrical stress among the healthy and the defective insulation parts due to different dielectric properties of the healthy and defective parts of insulation.

Multi-core model for nanoparticle – polymer interfaces



Multicore Tanaka model for nanoparticle−polymer interfaces

- Simplified term of a multi-layered core model;
- It can be understood as some more detailed structures of the interaction zones;
- it is a working hypothesis;
- A nano-particle of several tens nm in diameter is surrounded by an interfacial layer of the same order of dimension to be connected to an outside polymer matrix;
- This model applies to PD resistance characteristics of polyamide layered silicate nanocomposites, and is recognized as useful.

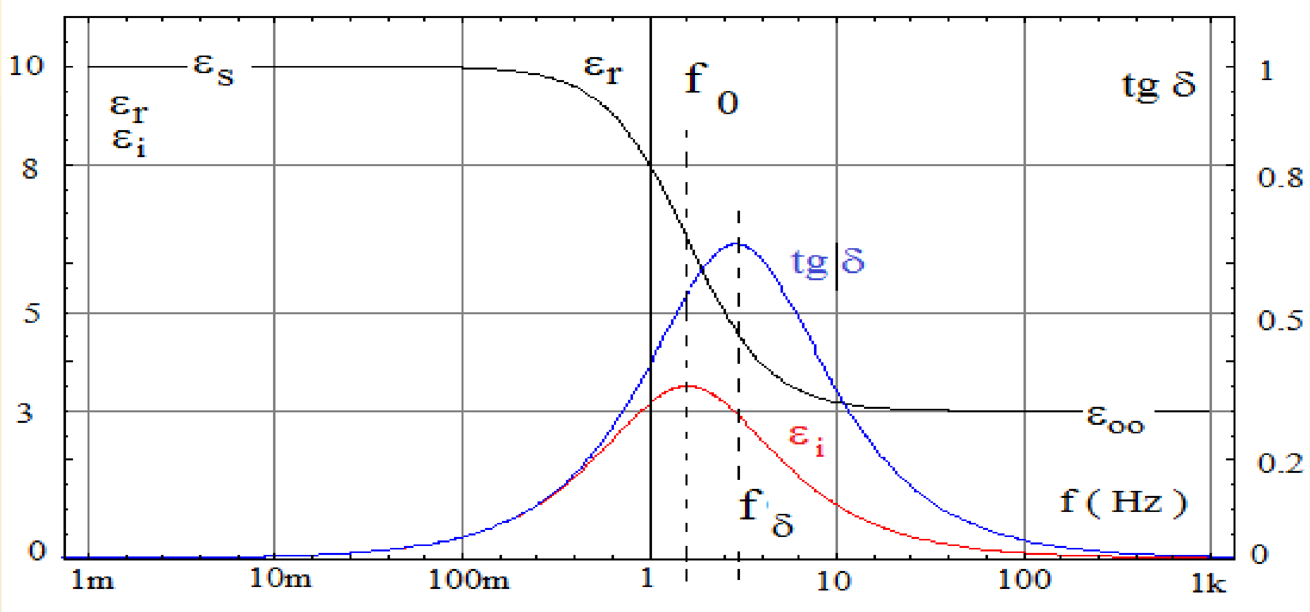
Complex permittivity

Debye model

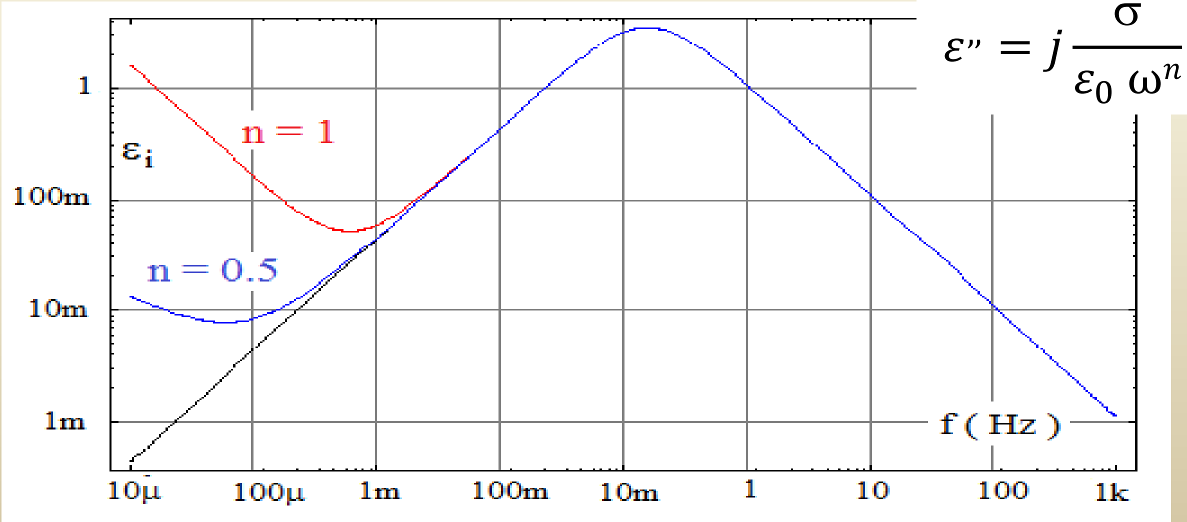
$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + j\omega\tau}$$

Cole-Cole model

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (j\omega\tau_0)^{(1-\alpha)}} + \frac{\sigma}{\varepsilon_0}$$



Dielectric with one relaxation process
(ε_s=10, ε_n=3, τ_0=0.1, ω_0 = 1/τ, ω_δ = (1/τ)√(ε_s / ε_∞)).



$$\varepsilon'' = j\,\frac{\sigma}{\varepsilon_0\,\omega^n}$$

Nanocomposites

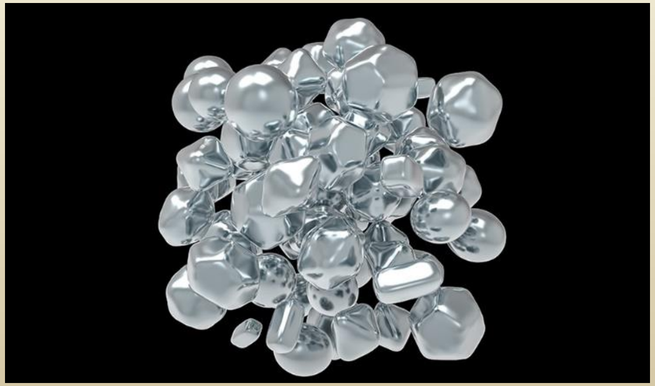
- Interesting electrical properties represent the epoxy based nanodielectric systems ⇨ the introduction of nanofillers to the pure epoxy resin demonstrate several advantages opposite to pure epoxy resin without nanofillers;
- Studies carried out in recent years clearly shows ⇨ the nanocomposites have exhibited markedly improved mechanical, thermal, optical and physic-chemical properties, owing to the nanometer-size particles obtained by dispersion, when compared with the pure polymers;
- The defects (voids and cavities) which are formed in solid insulating materials have generally a lower dielectric strength that may promote the formation of electrical discharge under normal operating conditions ⇨ followed the erosion of solid dielectric and its ultimate failure.
- The mixing of conductive nanofillers in polymer matrix can significantly improve the dielectric constant of composites when the filler content approaches the percolation threshold.

Polyurethane and nanoparticles

For sample preparation, a two-component PU (the VUKOL 022 and hardener agent Vukit M from VUKI a.s.) potting compound has been used.

Specific parameters of Zinc Oxide (ZnO):

- Purity: 99+%
- Average particle size: 20 nm
- Morphology of particles: spherical
- Specific surface area: ≥ 40 m^2/g
- Bulk density: 0.1-0.2 g/cm^3
- Color: white
- Loss on drying (110 °C/2h): ≤ 1.0 wt%
- Loss on calcination (850 °C/2h): ≤ 3.0 wt%.

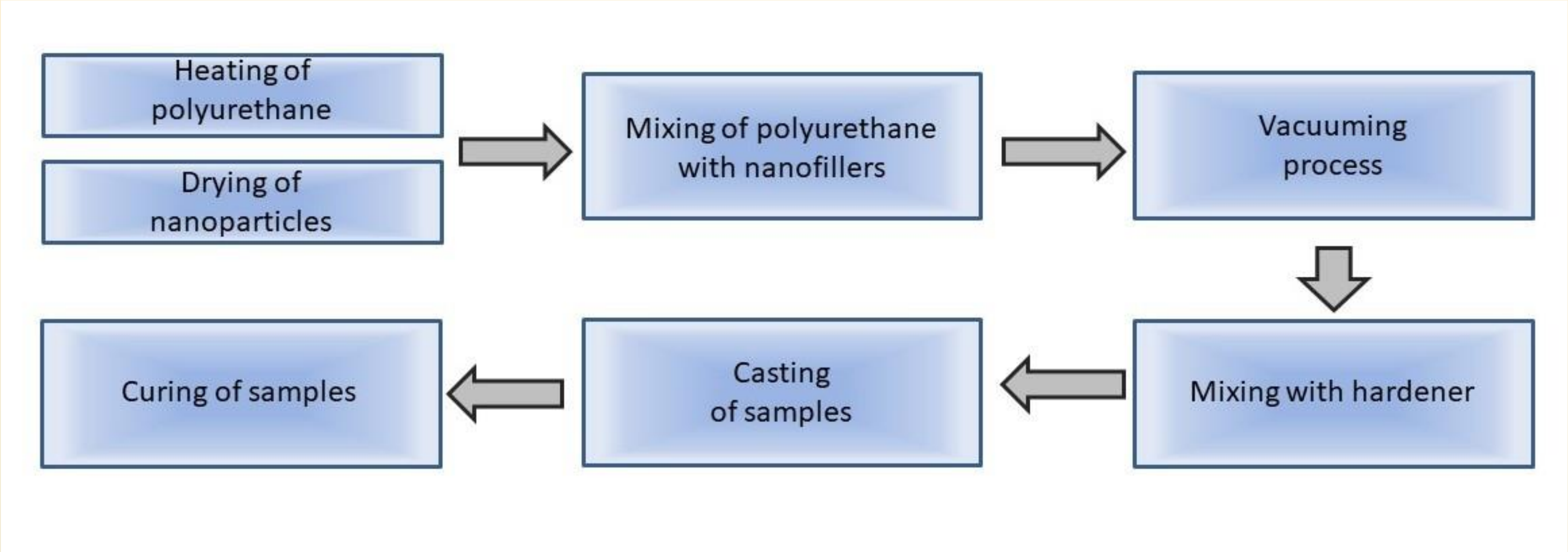


Name	Purity (%)	Radius (nm)	Surface treatment
MgO	≥99	20	-
TiO_2	≥96	20	$SiO_2 + C_{19}H_{36}O_2$
n-SiO_2	≥99	20	-
d-SiO_2	≥98	20	$C_2H_6Cl_2Si$
f-SiO_2	≥98	20	$C_{10}H_{20}O_5Si$

Purity, average size, and surface treatment information for the nanoparticles (NPs) used.

Preparation of samples (VUKOL 022 + x.y wt. % nanoparticles)

In the laboratory conditions the preparation of epoxy nanocomposites was done by method of direct dispersion.



The sample production process can be divided into several parts:

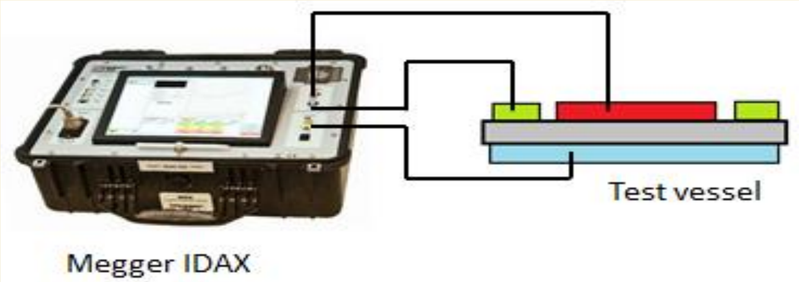
- Nanoparticle filler was heating for 24 hours for losing of surface humidity.
- The epoxy resin was heated to a selected temperature for better viscosity before the mixing.
- Filler and epoxy resin were mixed together for 3 hours on a magnetic stirrer.
- Vacuuming process: 5 hours and was used for the venting of the mixture and air bubble removal.
- Mixing with hardener agent in ratio 100:37.
- The created mixture was poured flat sample with square shape.

Measurement of the dielectric parameters

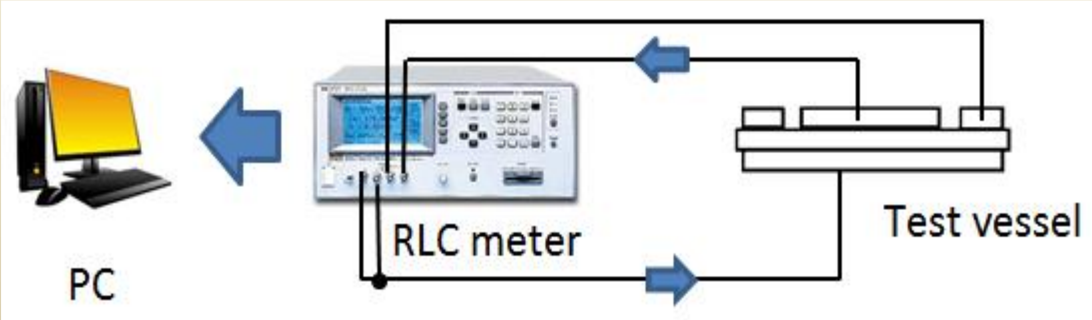
- Studies of the complex relative permittivity of nanocomposities as a function of the frequency of electric field and temperature are one of the basic features of dielectrics.

- We measured by IDAX 350 and LCR Meter device the dielectric properties including relative permittivity, *tan δ* and imaginary part of the complex relative permittivity at various temperatures 20°C to 120°C and frequencies:

  - IDAX 350 from 1 mHz to 10 kHz.

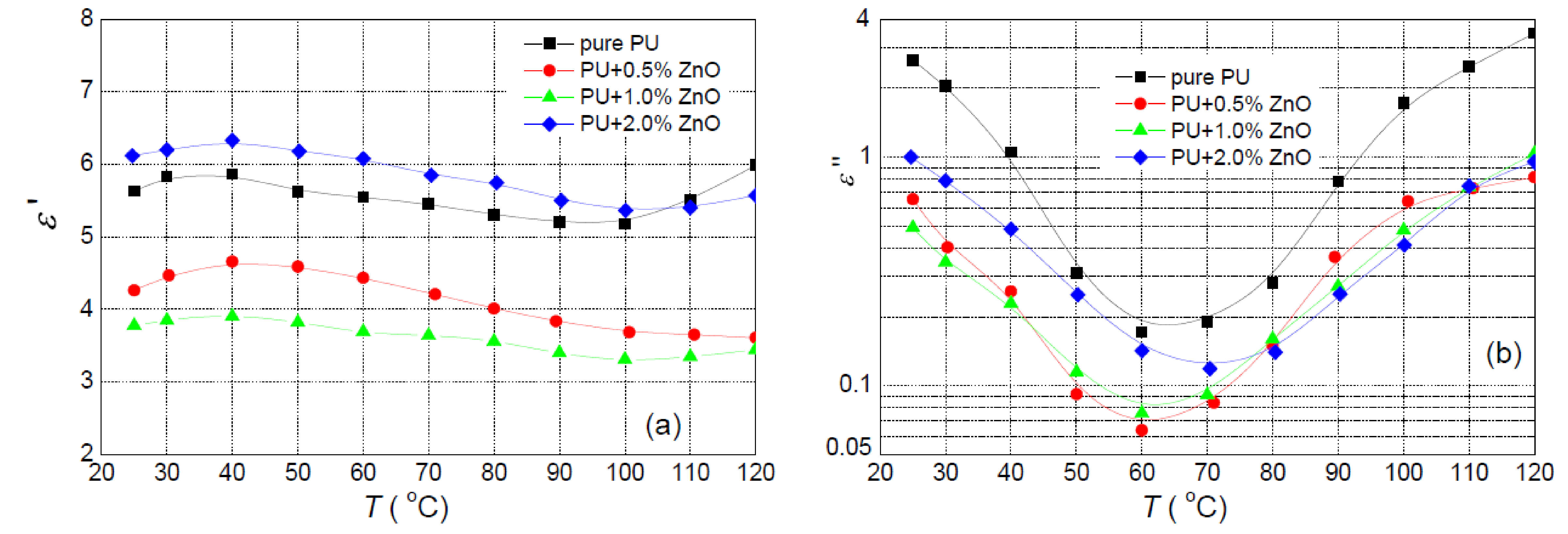


  - LCR Meter OT 7600 Plus - from 100 Hz to 2 MHz.



Novocontrol Alpha A from 0,5 Hz to 1 MHz at temperature range -60 °C to 100 °C (University of West Bomemia).

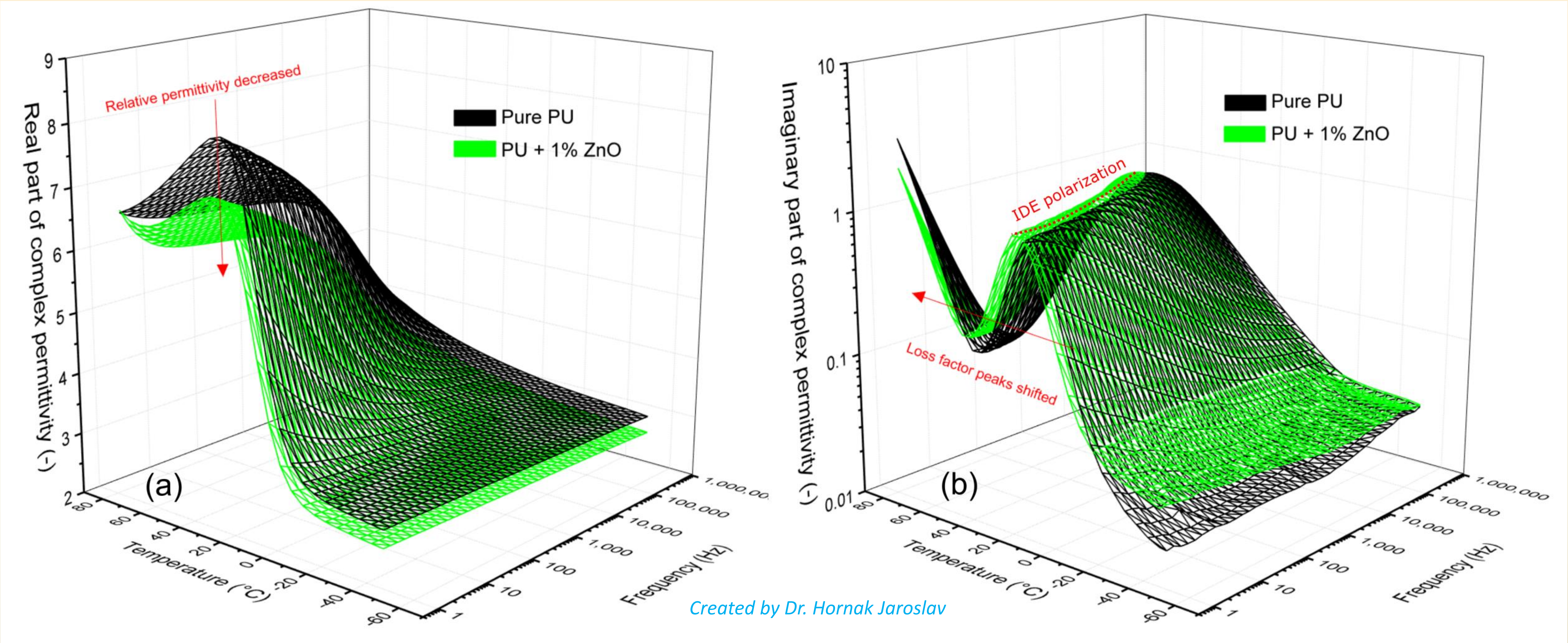
Experimental results obtained by doping of ZnO to the pure PU



*Temperature dependence of (**a**) the real and (**b**) imaginary parts of the complex permittivity for polyurethane resin and its various mixtures with ZnO nanoparticles measured at frequency 50 Hz.*

Kúdelčík Jozef; Hardoň Štefan; Trnka Pavel; Michal Ondrej; Hornak Jaroslav, *Dielectric responses of polyurethane/Zinc Oxide blends for dry-type cast cold-curing resin transformers,* ***POLYMERS (Q1),*** Volume: 13 Issue: 3, Article Number: 375, Publikované: FEB. 2021.

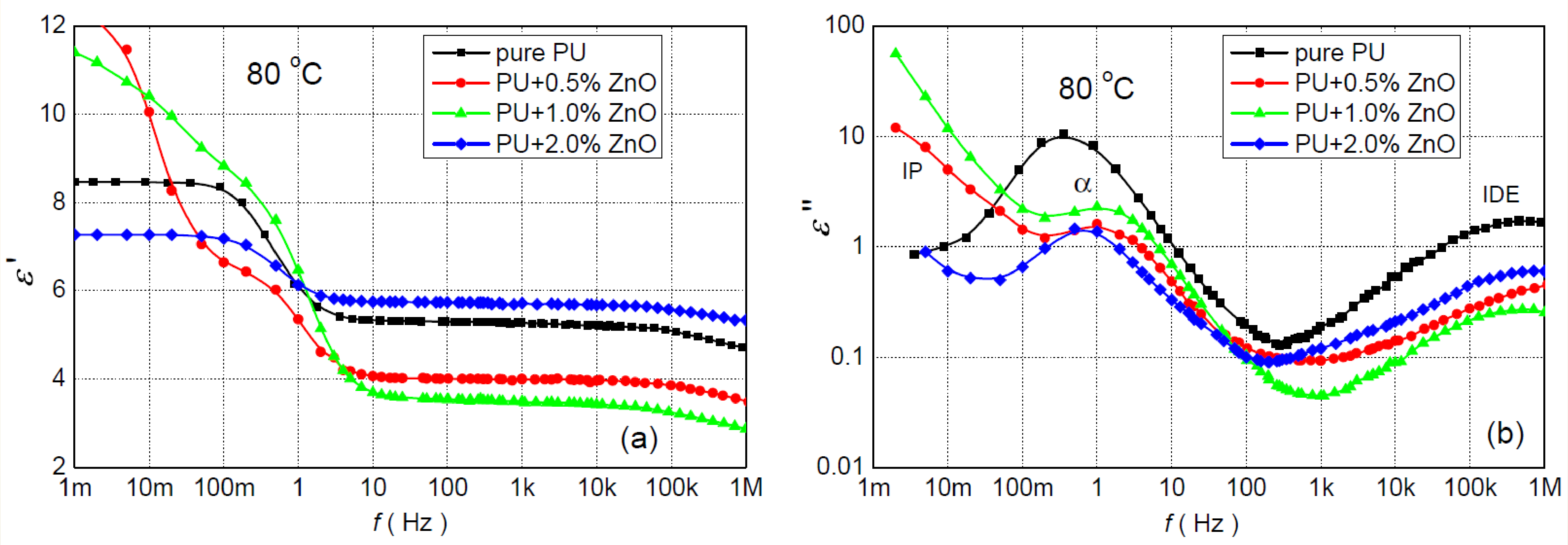
Complex permittivity versus frequency and temperature



*The real (**a**) and imaginary (**b**) part of complex permittivity versus frequency and temperature for the pure PU resin and its mixture with 1.0 wt.% ZnO.*

Kúdelčík Jozef; Hardoň Štefan; Trnka Pavel; Michal Ondrej; Hornak Jaroslav, *Dielectric responses of polyurethane/Zinc Oxide blends for dry-type cast cold-curing resin transformers,* ***POLYMERS (Q1),*** Volume: 13 Issue: 3, Article Number: 375, Publikované: FEB. 2021.

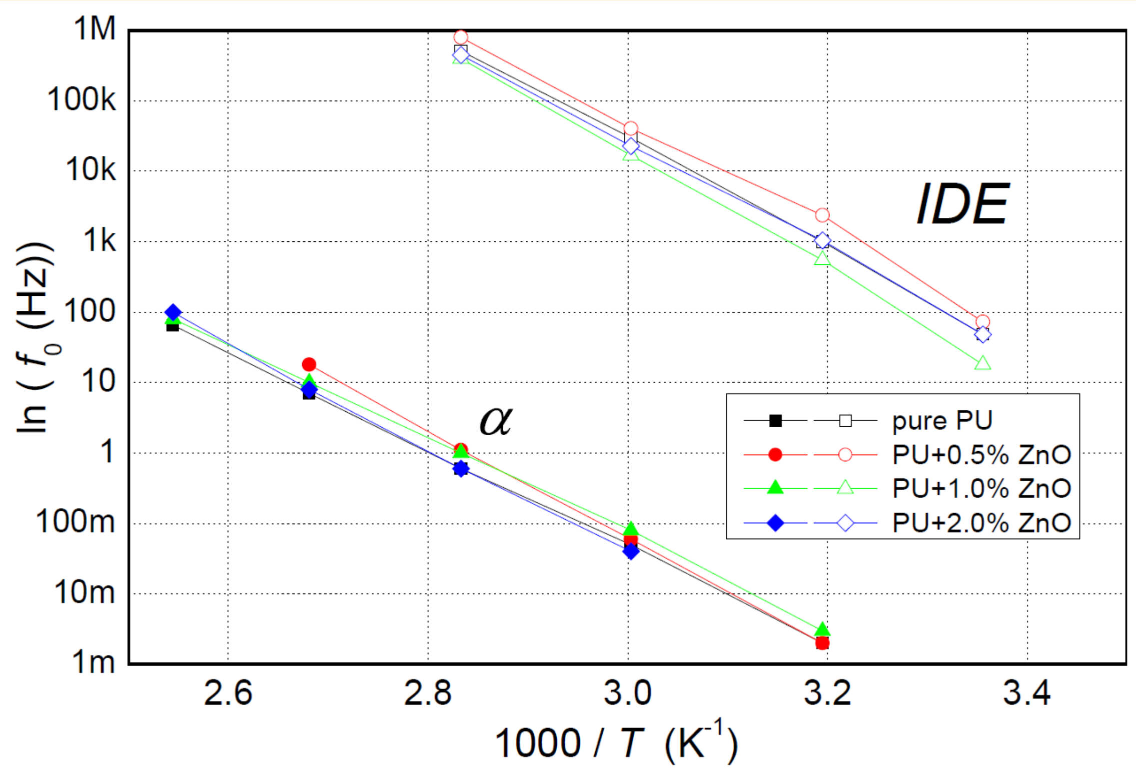
The permittivity spectra at temperature 80 °C (a normal temperature of a Cast Resin Dry Type Transformer)



The frequency dependence of (a) the real and (b) imaginary parts of the complex permittivity for polyurethane resin and their various nanocomposites at temperature 80 °C.

Kúdelčík Jozef; Hardoň Štefan; Trnka Pavel; Michal Ondrej; Hornak Jaroslav, *Dielectric responses of polyurethane/Zinc Oxide blends for dry-type cast cold-curing resin transformers*, ***POLYMERS (Q1),*** Volume: 13 Issue: 3, Article Number: 375, Publikované: FEB. 2021.

Relaxation map of pure PU and its nanocomposites



Relaxation map of pure PU and its nanocomposites based on measured developments of complex permittivity and corresponding local maximum.

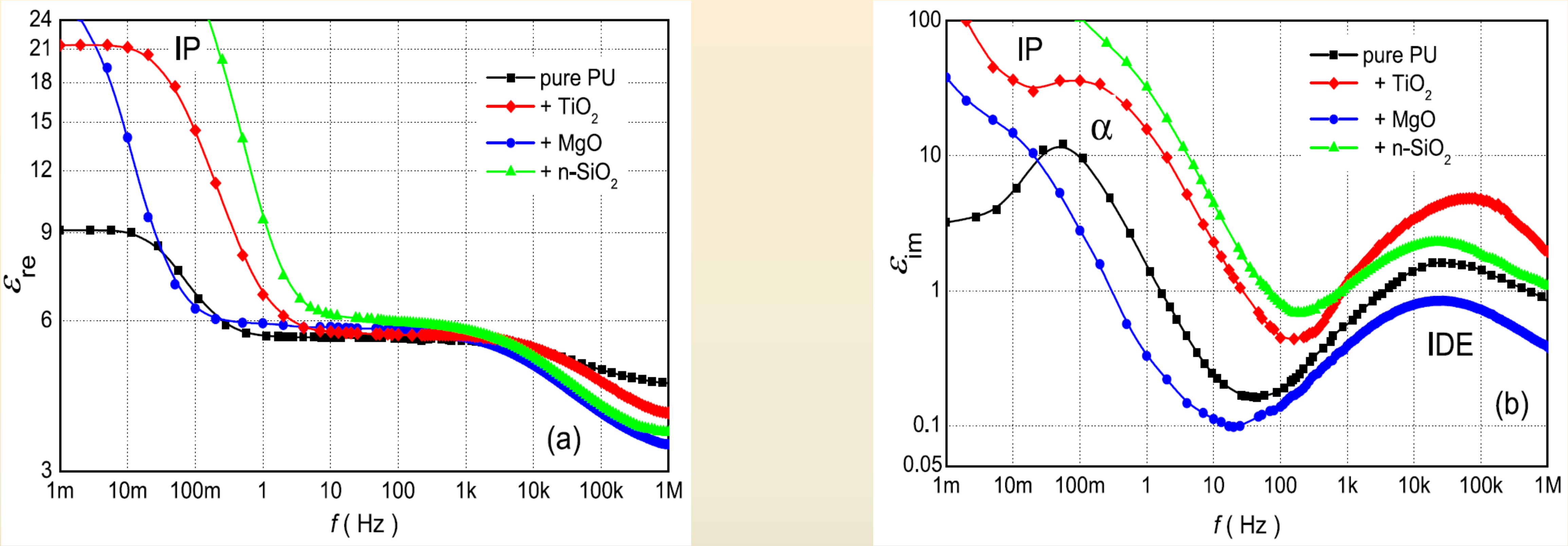
Conclusion

The complex dielectric permittivity, dissipation factor, and DC electrical conductivity of the nanocomposites were measured in the temperature range from 20–120 °C. 0.5 and 1.0 wt.% nanoparticles caused a decrease in the real permittivity as pure PU resin. This decrease was caused by the presence of highly immobile PU chains in the interfacial regions around nanoparticles.

The presence of local relaxation peaks in the imaginary permittivity and dissipation factor spectra of the nanocomposites confirms the absorption of energy given to the system by the chain segmental dynamics of the polymer and nanoparticles.

Kúdelčík Jozef; Hardoň Štefan; Trnka Pavel; Michal Ondrej; Hornak Jaroslav, *Dielectric responses of polyurethane/Zinc Oxide blends for dry-type cast cold-curing resin transformers,* ***POLYMERS (Q1),*** Volume: 13 Issue: 3, Article Number: 375, Publikované: FEB. 2021.

Experimental results obtained by doping various types of nanoparticles to the pure PU



The frequency dependence of the real (a) and the imaginary (b) part of the complex permittivity for PU and its mixtures of 1 wt.% with various NPs at 60 °C.

Kúdelčík Jozef; Hardoň Štefan; Hockicko Peter; Kúdelčíková Mária; Hornak Jaroslav; Prosr Pavel; Trnka Pavel, Study of the complex permittivity of a polyurethane matrix modified by nanoparticles, **IEEE ACCESS (Q1)**, VOLUME 9, 2021, Publikované: MAR. 2021.

Conclusion

- Dielectric spectroscopy for the study of PU NCs with various surface modications of SiO_2 and types of NPs as fillers was used.

- This can help to understand basic issues related to the role of additives, their surface modication, and interactions with a two-component PU matrix.

- For a description of the observed changes in the dielectric properties of PU NCs, the multi-core model of the NCs and the influence of a local electric eld on the trapped charges were used.

- In the case of the *d*-SiO_2 filler, the complex permittivity was lower than for other fillers.

- The effects of the α-relaxation and IDE relaxation processes were identified with dielectric spectroscopy.

- The IP and charge multiplication of α -relaxation process for all types of NPs caused the shifts of the peak and a marked increase in the relative permittivity, $\epsilon''re$, for sub-Hertz frequencies.

Thank you for your attention