The use of nanoparticles in polymeric insulating materials.

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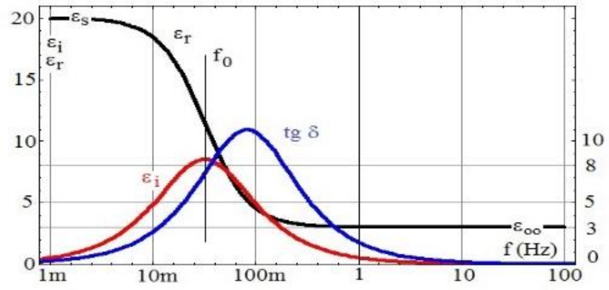
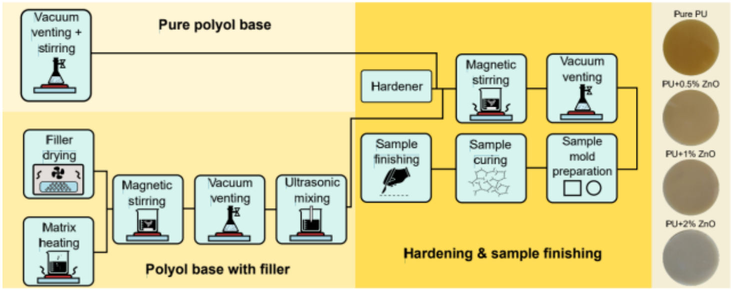
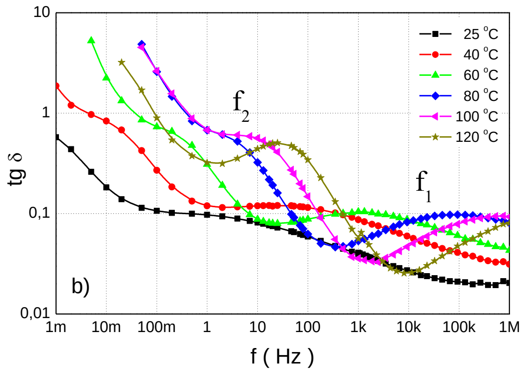
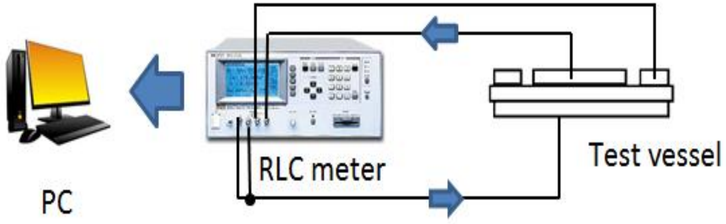
Content of the lecture









1. Polymers

- Polymers have unique properties and characteristics that make them **useful in a wide range of applications**. Some key features of polymers include their high molecular weight, versatility in terms of physical and chemical properties, and the ability to be molded or shaped into different forms.
- Overall, polymers **play a crucial role in various industries**, including packaging, automotive, construction, electronics, healthcare, and many more. Their versatility and customizable properties make them essential materials in modern society.
- The properties of polymers can be tailored by adjusting the monomer composition, molecular weight, and processing conditions during polymerization. This allows for **the creation of polymers with specific characteristics**, such as strength, flexibility, thermal stability, chemical resistance, and electrical conductivity.
- **A polymer is a large molecule composed of repeating subunits called monomers**. These monomers are chemically bonded together to form a long chain-like structure. Polymers can be found in various forms, including plastics, rubber, fibers, and even biological macromolecules like proteins and DNA.
- Polymers can be classified into different categories based on their structure, such as linear polymers, branched polymers, and cross-linked polymers. **They can also be categorized based on their origin**, such as **synthetic polymers** (man-made) and **natural polymers** (derived from natural sources).

Polyurehanes

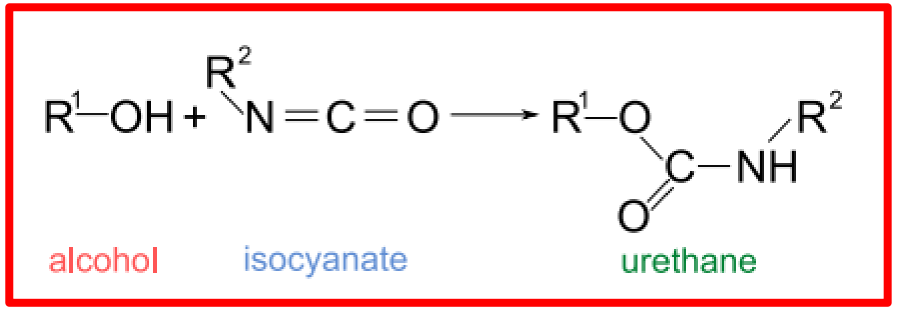
Polyurethanes (**PUR**) - significant group of polymers with a wide range of uses. In 2019, the global annual production reached about 25 million tons (about 6% of all organic polymers).

The basic advantage of PUR is that, at a reasonable price, it is possible to achieve a very wide variability of properties and parameters with simple interventions in the composition, while the polymerization reaction itself is usually carried out at room temperature.

In practice, both foam PUR (hard, e.g. for thermal insulation in construction, ...) and compact PUR (without bubbles) - for the production of cast floors (and generally in construction - composites), and also electrical insulating materials (encapsulating or encapsulating transformers, terminal blocks, capacitors, electrical circuits, car batteries, etc.).

Two-component systems (**2K**) are materials consisting of two liquid or semi-liquid components (in separate packages). Mixing (at the point of application) creates a liquid reactive mixture in which a gradual chemical reaction takes place between the two components; the reaction forms a polymer.

In the case of **2K PUR** systems, component A is an organic polyol (polyhydric alcohol, usually with various additives) and component B is an isocyanate-based hardener. Chemically, the essence of curing is the addition reaction of the isocyanate groups in the hardener molecule with the hydroxyl groups of the polyol, in the sense of the general equation:



Additives - a desiccant (moisture absorber)
- a filler (ground inorganic materials).

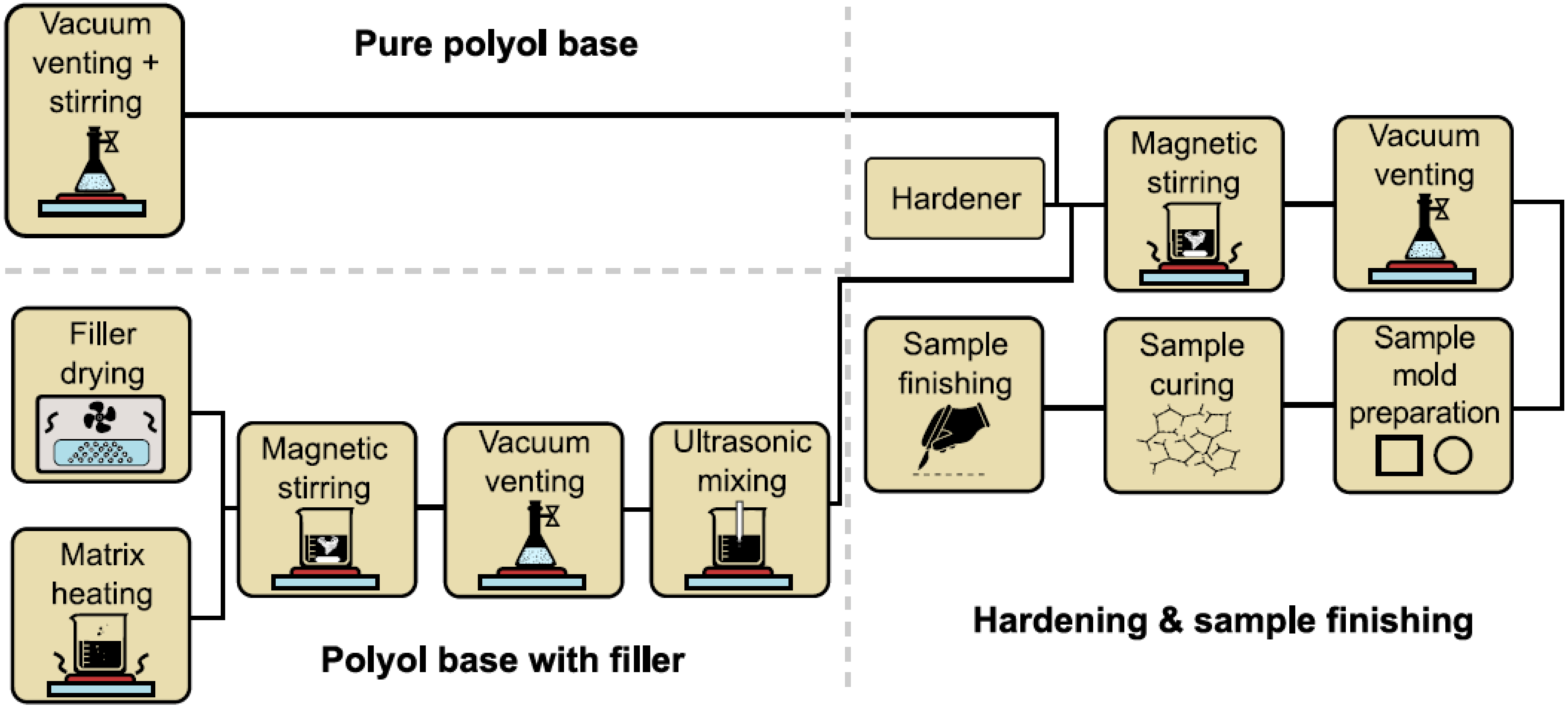
Improvent - mechanically strength, thermal conductivity, possibly suppress the material's flammability, or other properties.

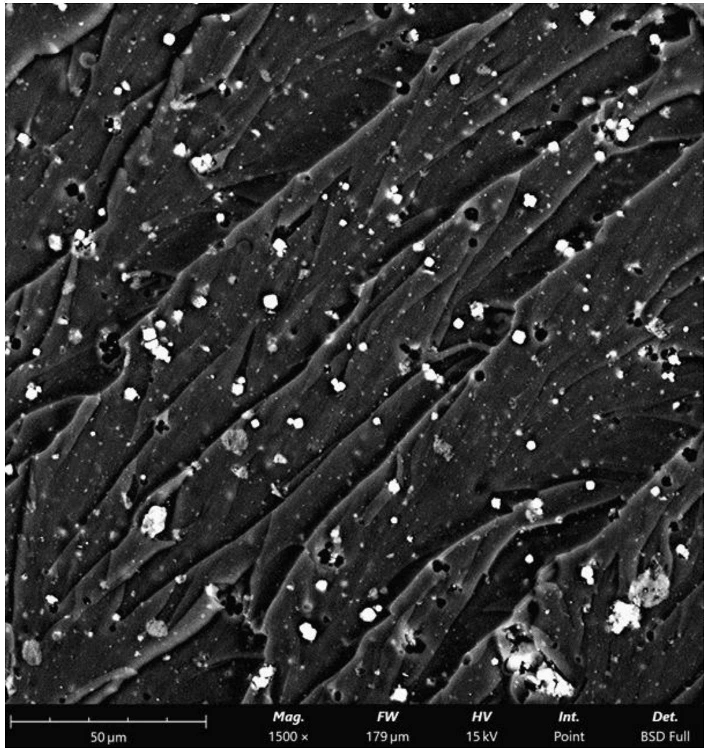
VUKOL N22 is **2K PUR** (resin + hardener) for potting, with low initial viscosity. The system hardens **at room temperature**. It is suitable for a wide range of applications. It contains only small amounts of inorganic fillers and is free of solvents **(VOC < 1 %)**. The hardened resin resembles hard rubber and belongs to medium hardness class of polyurethanes.

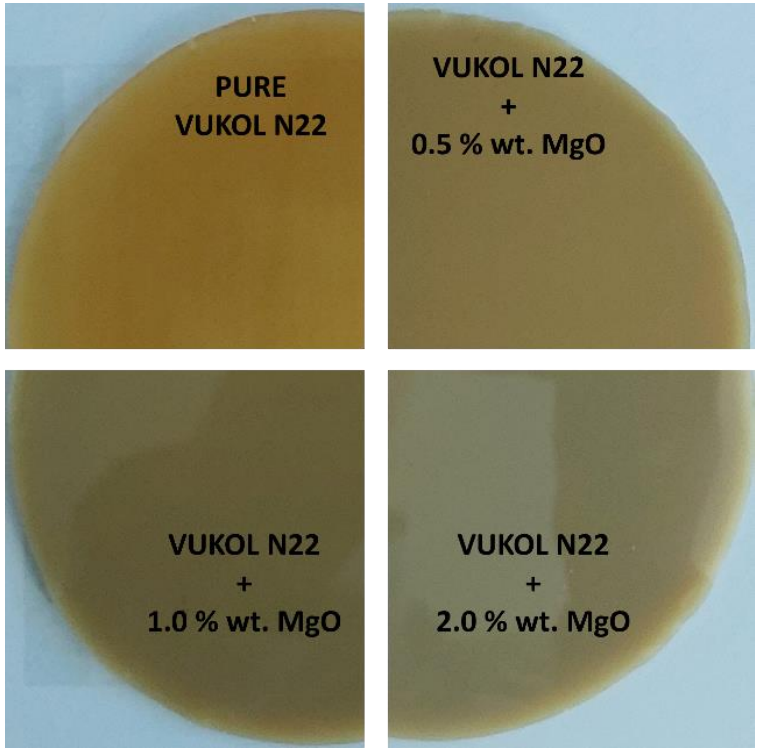
Some basic properties:

- thermal-class B (130 °C)
  - very good thermal-shock resistance
- good dielectric properties
  - Dielectric strength 20 – 25 kV/mm
  - Permittivity 4.2
  - tg δ 0.089
  - Thermal conductivity 0.22 W/mK
- favorable mechanical properties, no internal tension
- highly resistant to water
- bubble free castings
- solvent and halogen free system
- fire retardancy class V2/2 mm (according to UL94)
- available in natural (yellowish), black and pigmented versions (blue – approx. RAL 5005)

2. Preparation of samples





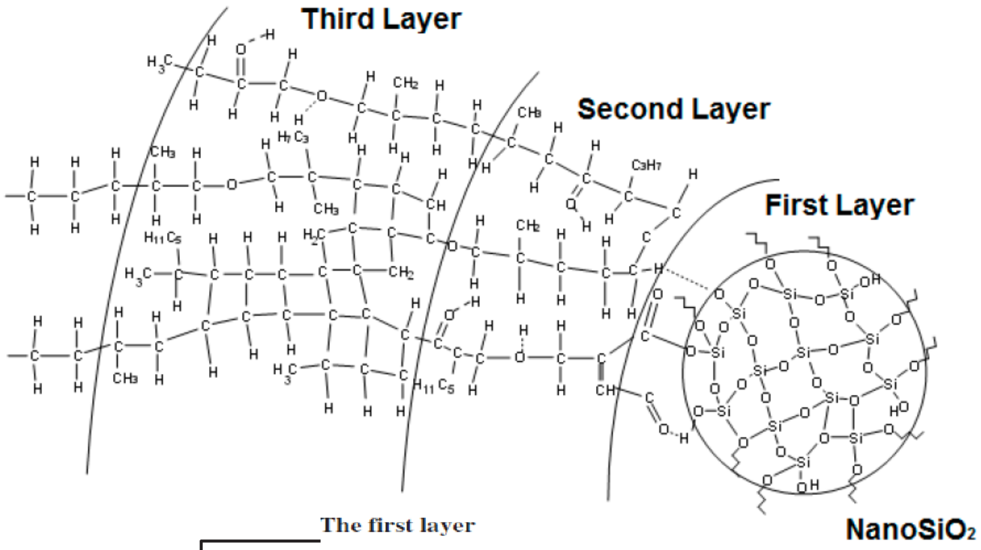


Particle dispersion analyse of PUR dopped with 2.0 % wt. MgO (the left) and colour change of investigated PUR composites with different concentrations of MgO (the right).

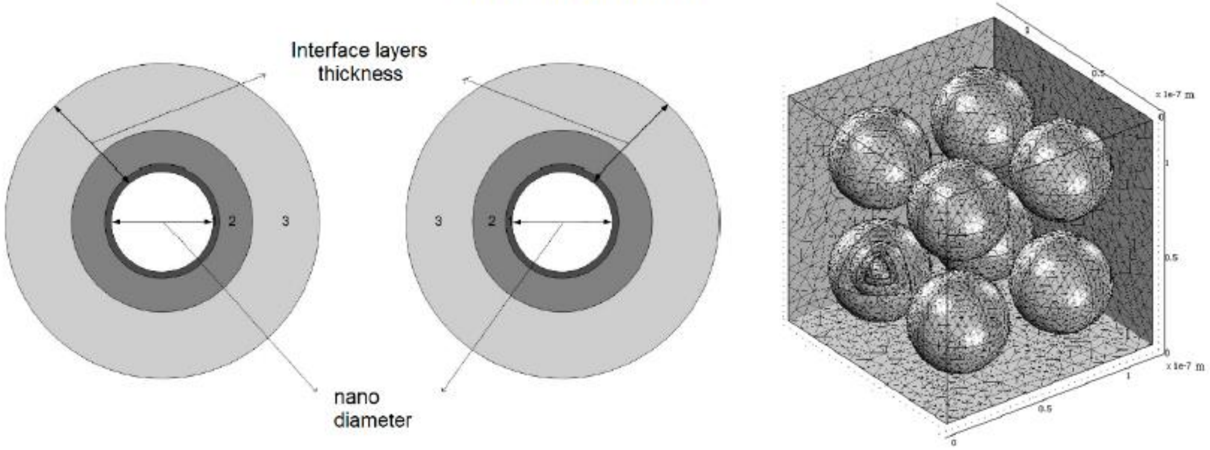
Parameters of nanoparticles

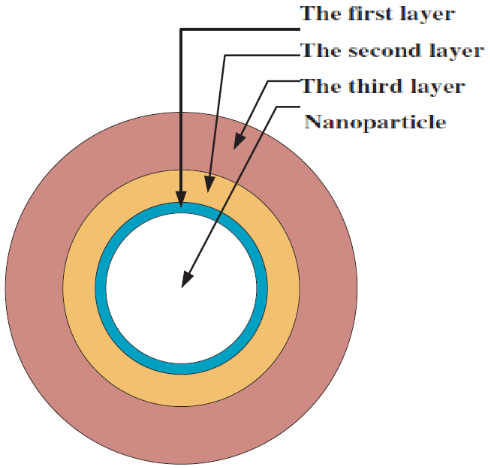
	Magnesium Oxide	Zinc Oxide	Aluminium Oxide
Purity (%)	>99	>99	99.97
Specific Surface Area (m^2/g)	60	40	180
Color	white	white	white
Bulk Density (g/cm^3)	0.1 – 0.3	0.1 – 0.2	3.95
pH value: 5.5-7.0	7.5 – 8.5	6.5 – 7.5	5.0 – 7.5

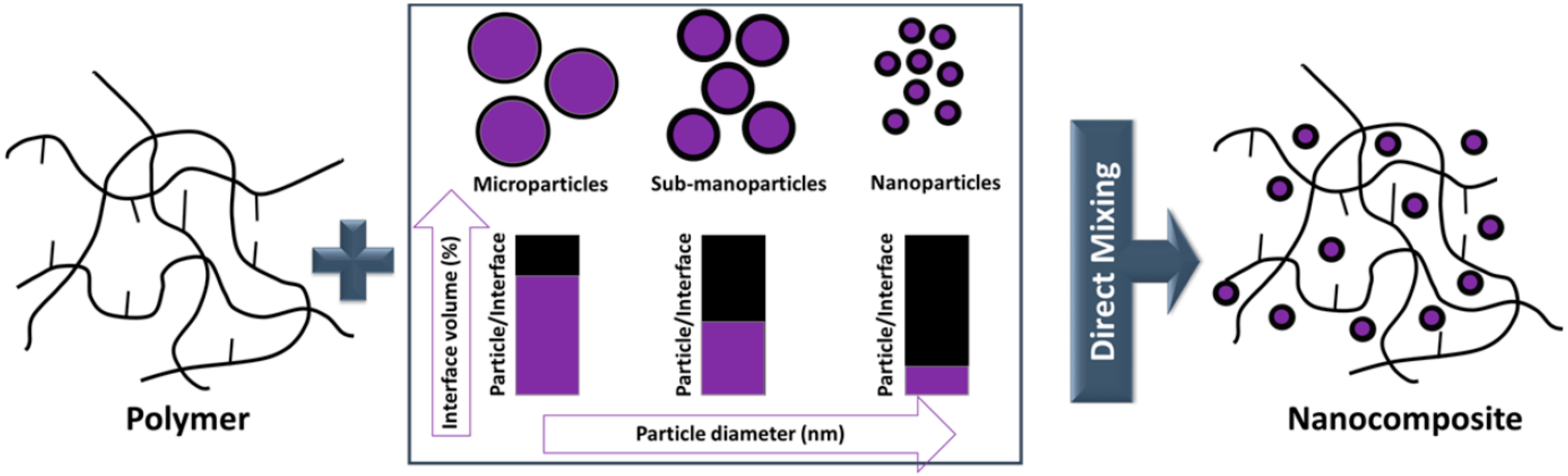
Incorporation of nanoparticles to polymers



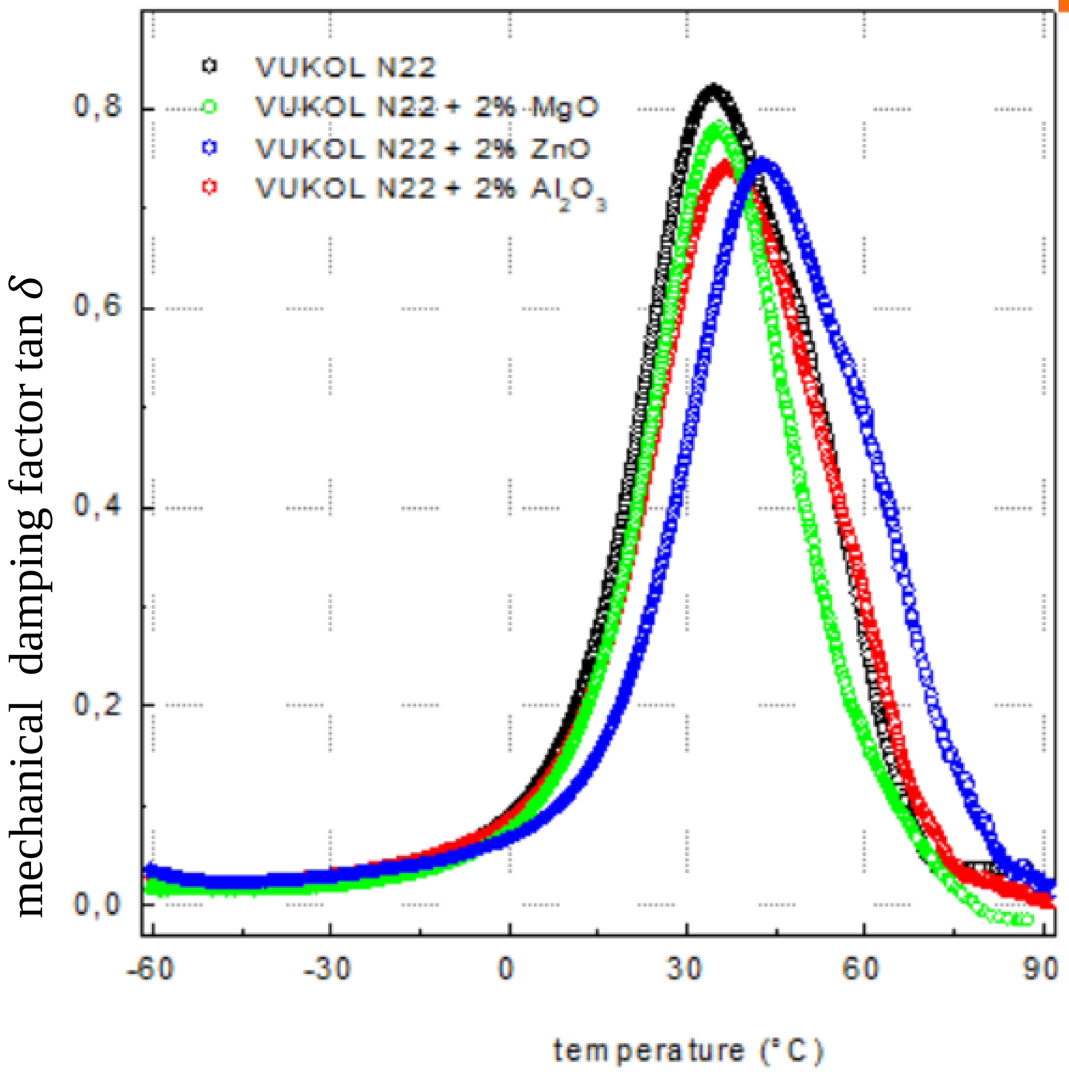
2 wt % LDPE/nano







3. Dynamic-mechanical analysis



	Al_2O_3	MgO	ZnO
% wt.	T_g (K)		
0	34.6	34.6	34.6
0.5	36.6	35.4	48.5
1	50.3	33.2	42.2
2	36.5	35.4	43.2

the peak magnitude of tan δ = the glass transition temperature Tg.

Tg - polymer chains in amorphous regions of polymer undergo a relaxation transition from a rigid structure to a rubbery state.

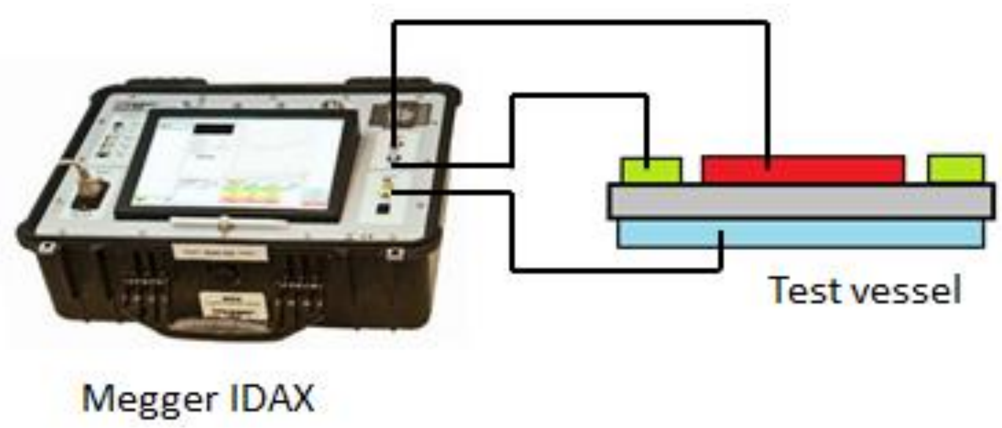
The shift of glass transition temperature to higher values usually reflects reduced-mobility of chains present in amorphous phase of polymer.

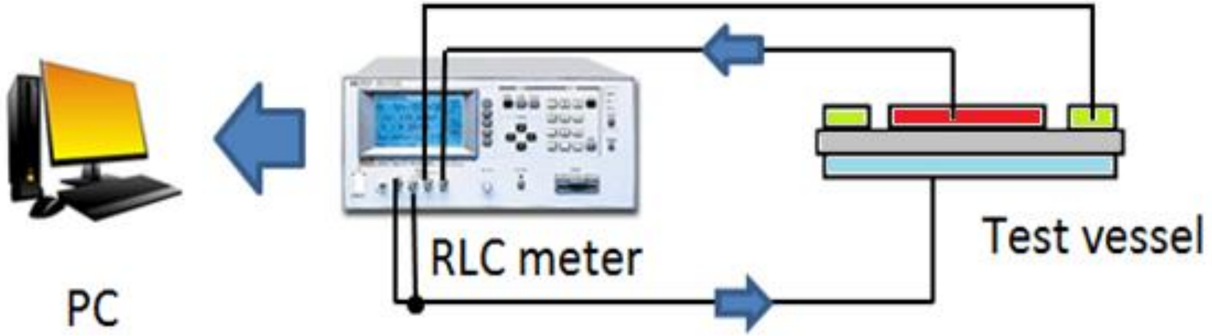
4. Dielectric frequency spectroscopy

- Temperature 20°C - 120°C

$$C = \varepsilon_r \varepsilon_0 \frac{S}{d} \qquad \mathrm{tg}\,\delta = \frac{1}{\omega\, R\, C} \qquad \mathrm{tg}\,\delta = \frac{\varepsilon''}{\varepsilon'}$$

IDAX 350
1 mHz to 10 kHz.





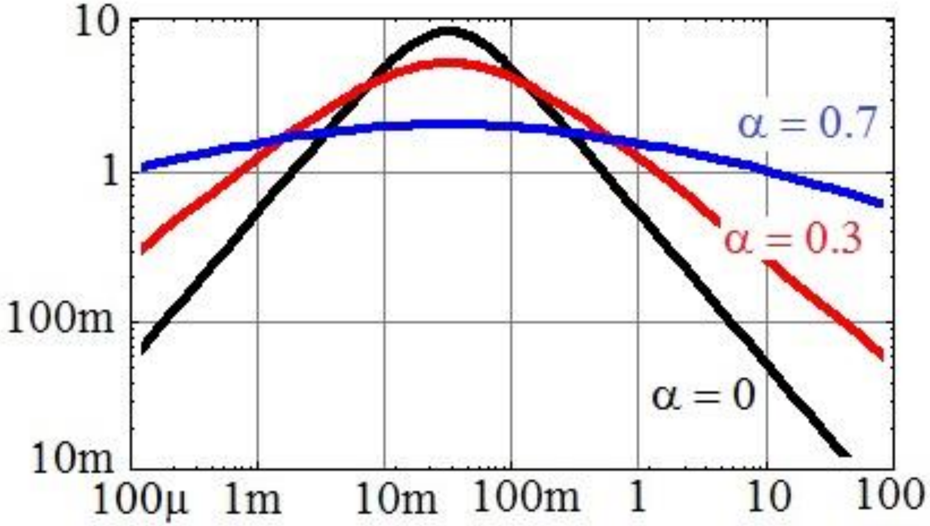
LCR Meter OT 7600 Plus
100 Hz to 2 MHz

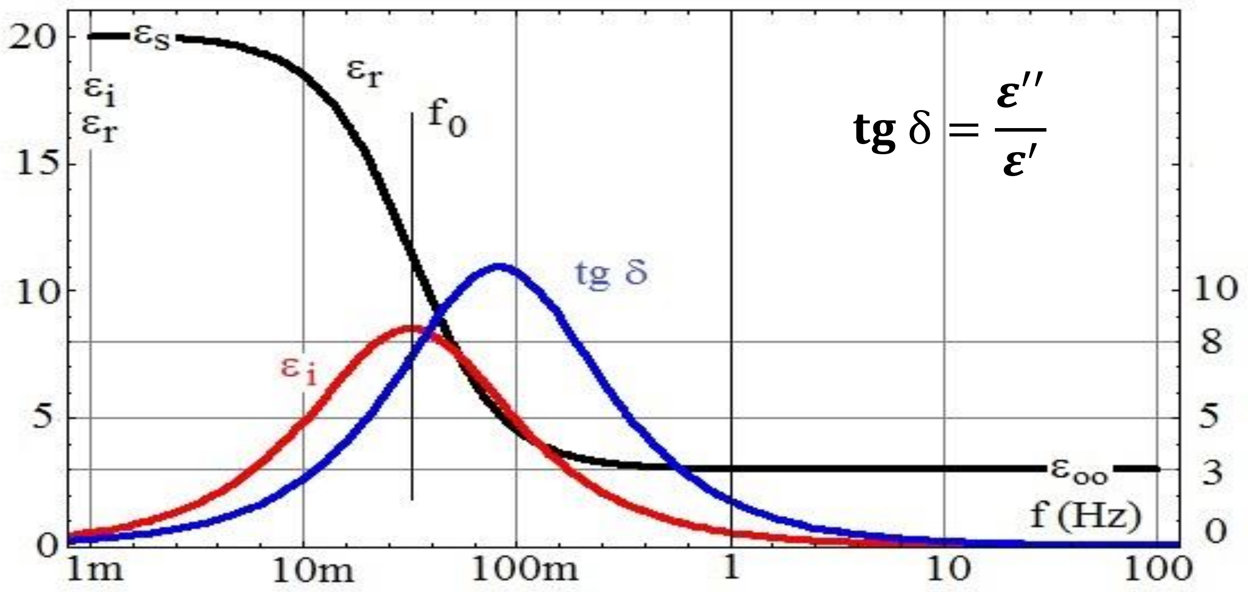
Complex permittivity

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

Debay / Cole-Cole model

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



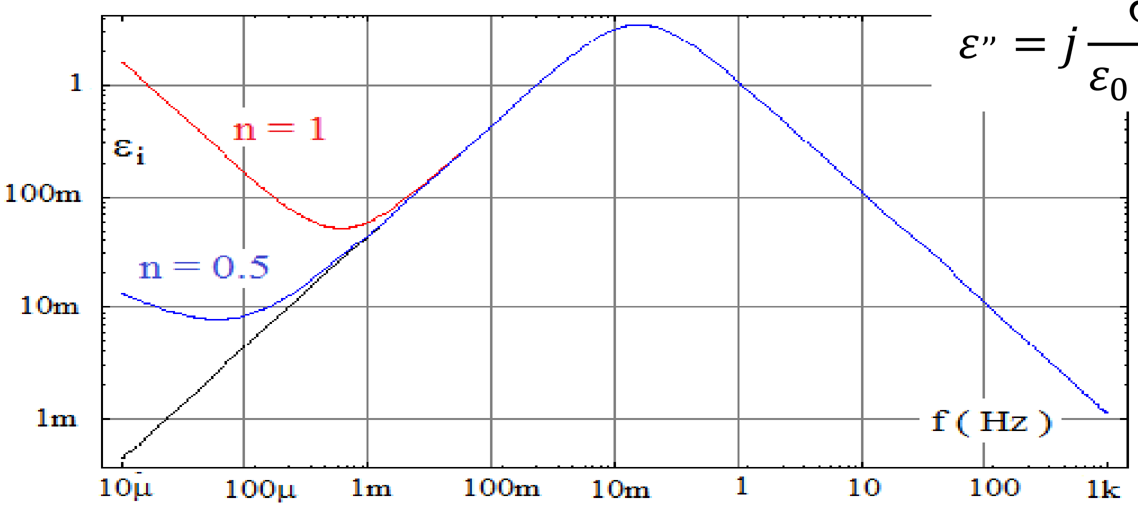


$$\mathbf{tg}\,\delta = \frac{\varepsilon''}{\varepsilon'}$$

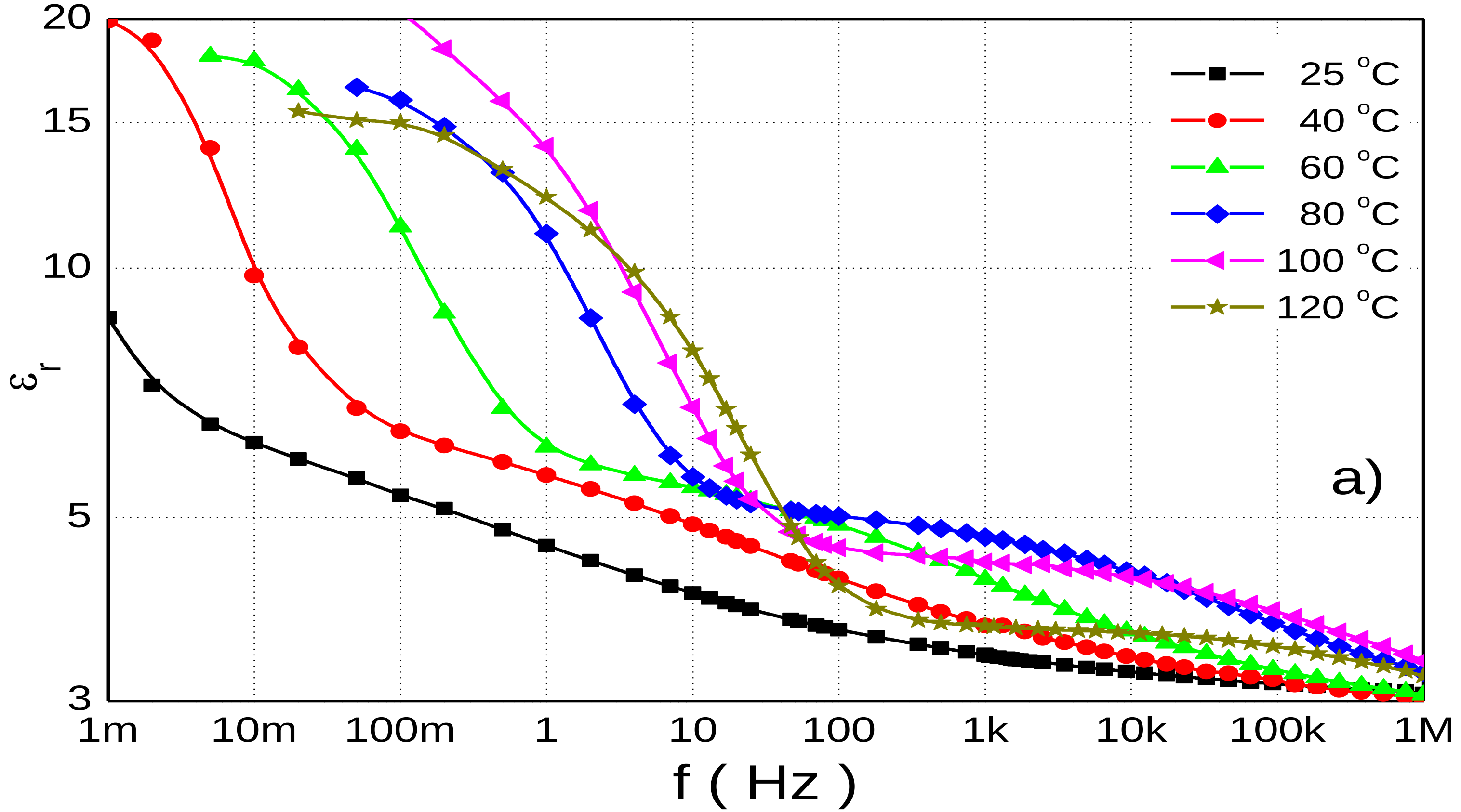
Dielectric with one relaxation process

(ε_s=20, ε_n=3, τ_0=5, $\omega_0 = 1/\tau$, $\omega_\delta = (1/\tau)\sqrt{(\varepsilon_s / \varepsilon_\infty)}$).

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



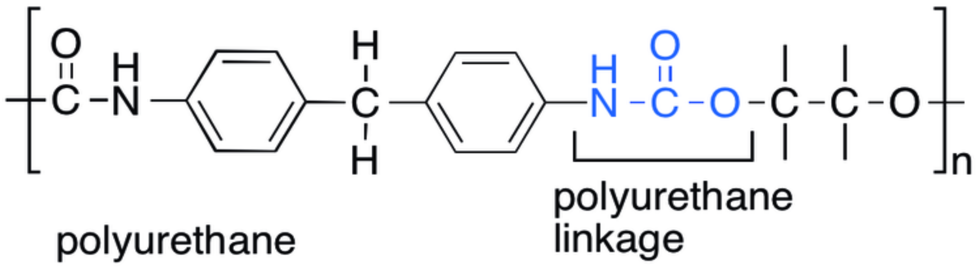
5. Experimental results

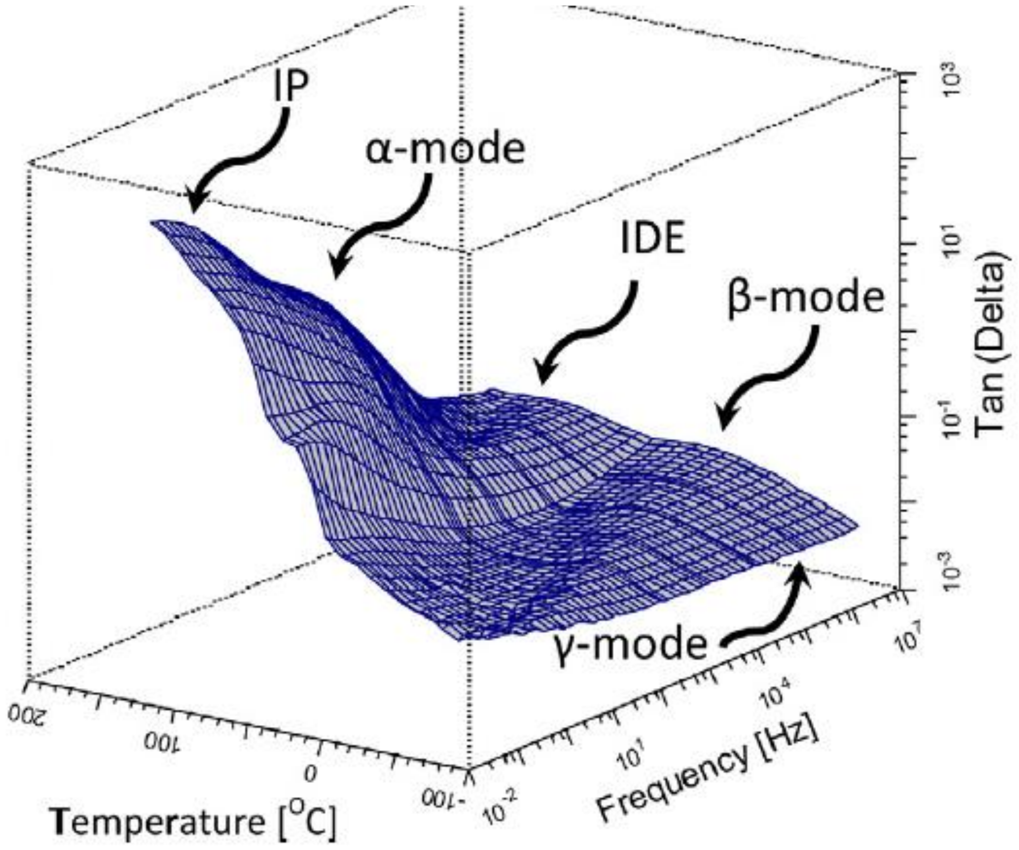


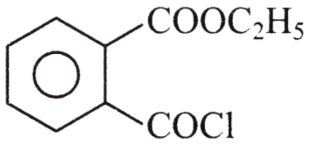
The frequency dependence of the real part of the complex relative permittivity for the polyeurethan with 0.5 wt% MgO nanoparticles at various temperatures.

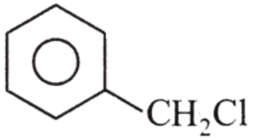
Relaxation processes

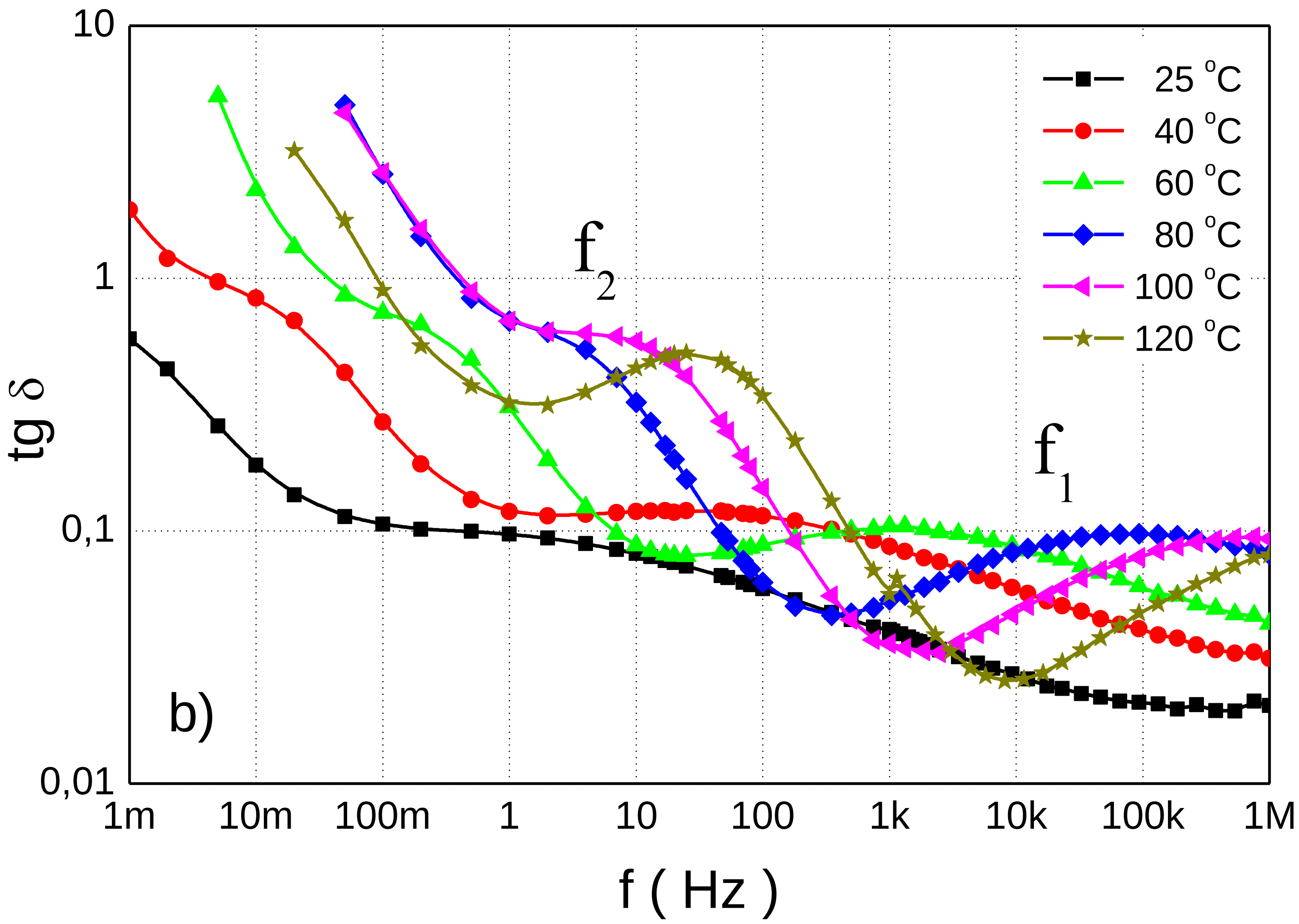
- **γ-mode** - rotation of methylene, hydroxyl ether groups of the main polymer chain and C-H units.
- Intermediate dipolar effect (**IDE**), between relatively fast and slow relaxation
- **β-mode** : orientation of polar groups around C-C chains
- **α-mode** by micro-Brownian segmental or motion of the entire polymer chain and associated with the glass transition temperature
- Interphase polarization (**IP**) at low frequencies and high temperatures = Maxwell-Wagner-Sillars effect





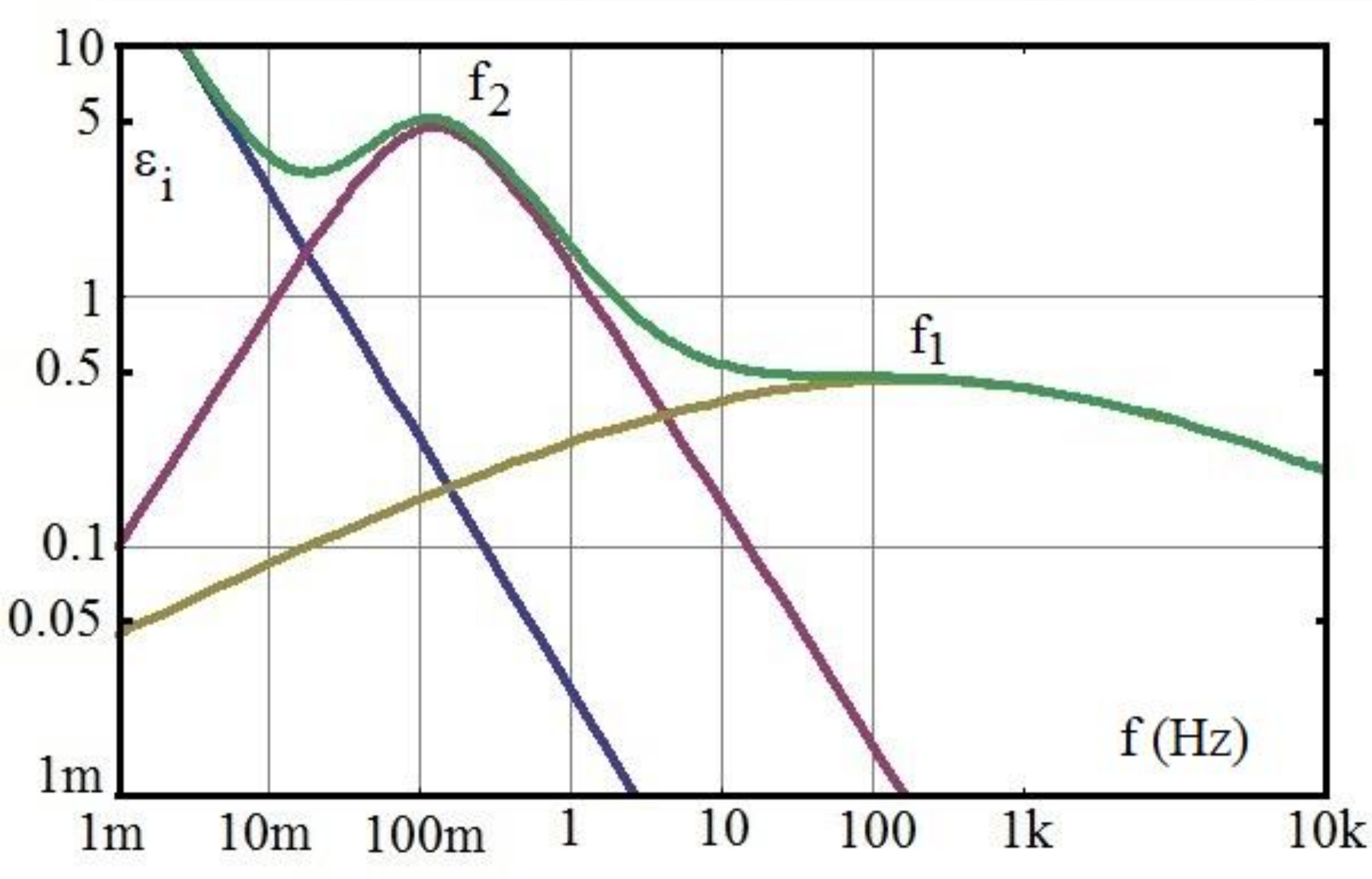






The dissipation factor for the polyeurethan with 0,5 wt% MgO nanoparticles at various temperatures.

- The first relaxation process corresponds to **IDE**-relaxation with **β-mode** - orientation or rotation of polar side groups around the C-C bond of PUR chains.
- The second low-frequency maximum correspond to **α-mode** - process is connected with the micro-Brownian motion of whole chains of PUR.

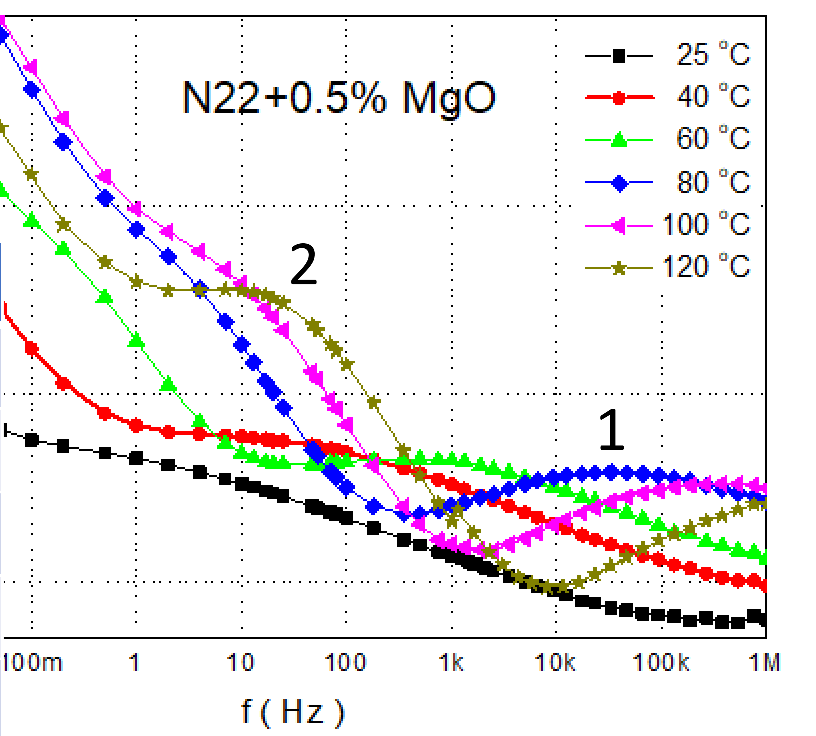


$$\varepsilon^* = \varepsilon_\infty - j\frac{\sigma}{\varepsilon_0\,\omega} + \sum_{k=1}^{2} \frac{\Delta\varepsilon}{1 + (j\omega\tau_{0k})^{(1-\alpha_k)}}$$

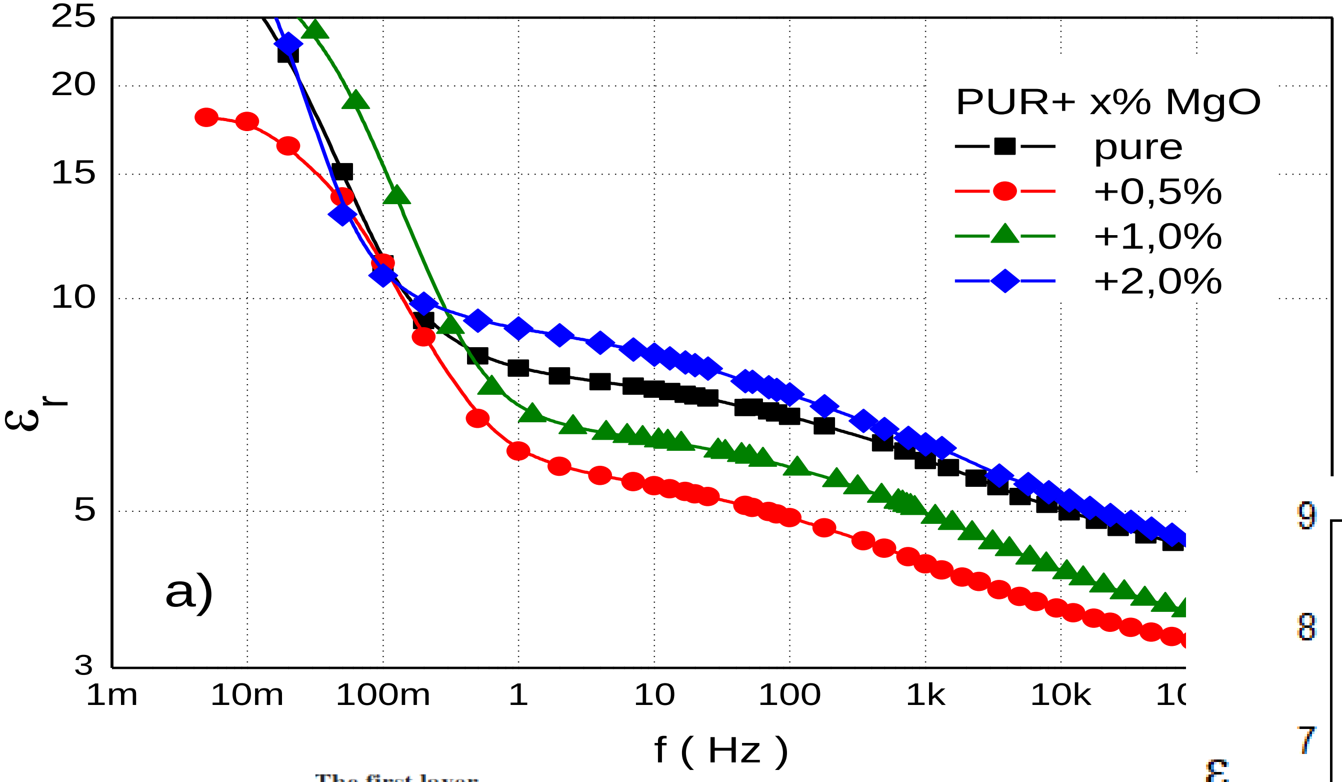
Cole-Cole fit of the imaginary part of the complex relative permittivity for polyurethane with 0.5% wt. of MgO nanoparticles at a temperature of 60 ^{o}C (green line), conductive losses (blue line), violet (α) and dark yellow (IDE) line - distribution functions of two relaxation processes.

$$\tau = \tau_0\, exp\{-E_A/k_B\ T\}$$

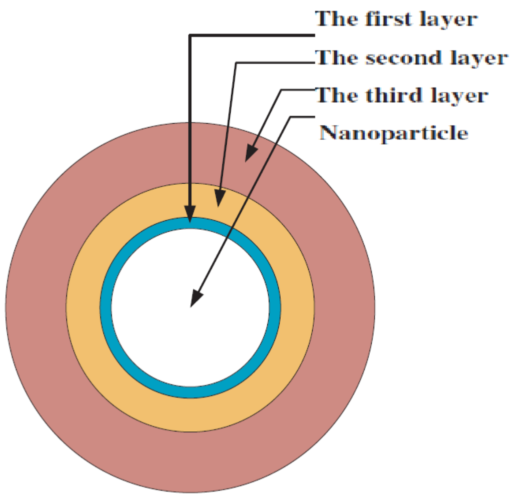
T (°C)	25	40	60	80	100	120
$\Delta\varepsilon_1$	5,02	5,74	3,82	2,09	1,09	0,56
ε_∞	3,01	2,80	2,82	2,90	3,13	2,89
τ_1 (s)	3,17	175m	932μ	3,91μ	0,742μ	0,185μ
f_{01}(Hz)	0.92	57,3	1.07k	255 k	1.34M	5,39M
α_1	0,34	0,33	0,30	0,45	0,70	0,86
σ (10^{-12})	0,17	1,93	24,9	217	268	58,9
$\Delta\varepsilon_2$	-	13,61	10,02	11,48	19,30	13,37
τ_2 (s)	-	33,65	1,29	0,16	0,17	0,05
f_{02} (Hz)	-	0,03	0,77	6,43	5,94	18,39
α_2	-	0,04	0,04	0,12	0,18	0,26

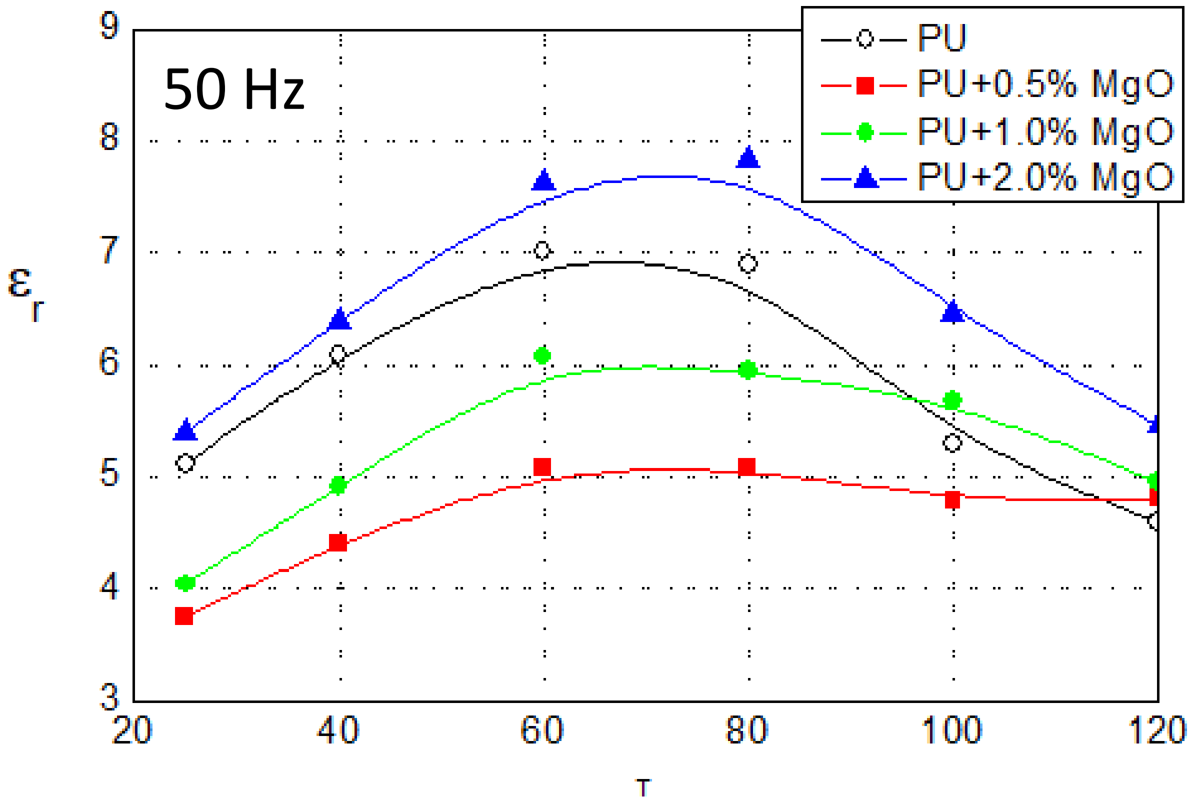


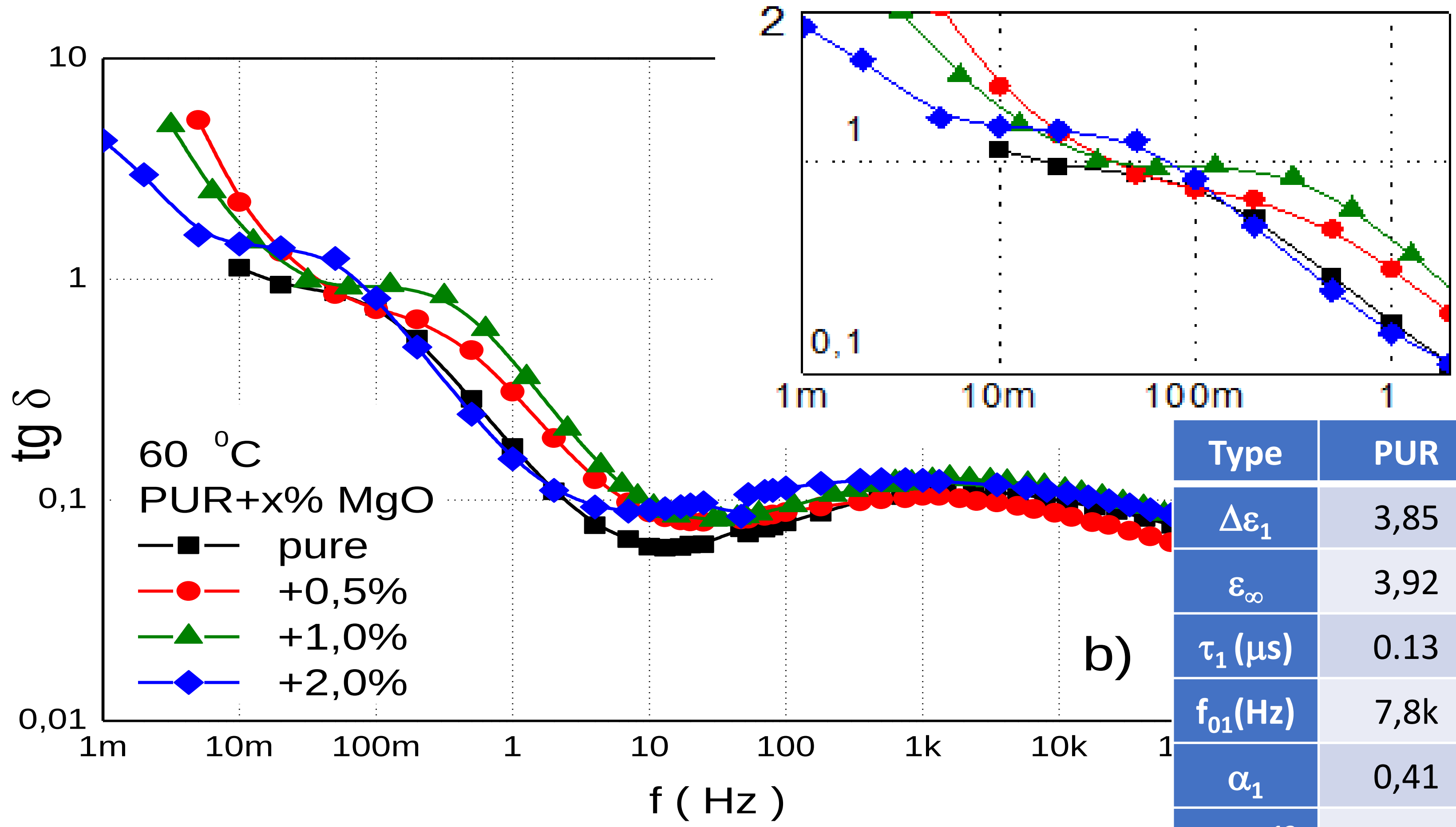
Parameters of Cole-Coleho model for nanocomposit (PUR with 0,5 % MgO) at different temperatures, where ε_∞ is high frequency limit for permitivity, σ(10^{-12} S/m) is DC conductivity, τ is relaxation time, $f_0 = 1/(2\pi\tau_0)$ and α is shape paremeter

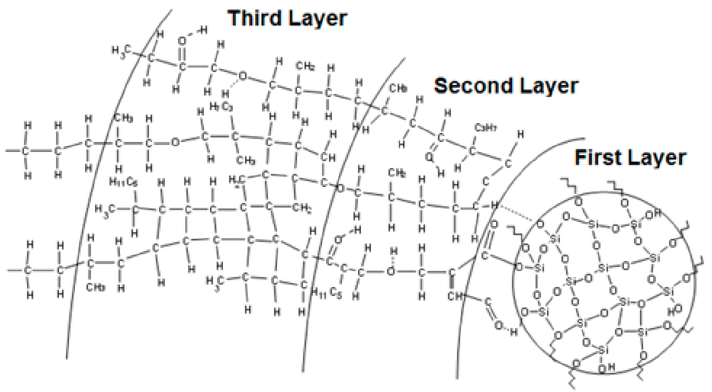


Frequency dependence of the real part of the real permittivity for polyurethane with different concentrations of MgO nanoparticles at temperature 60 °C.







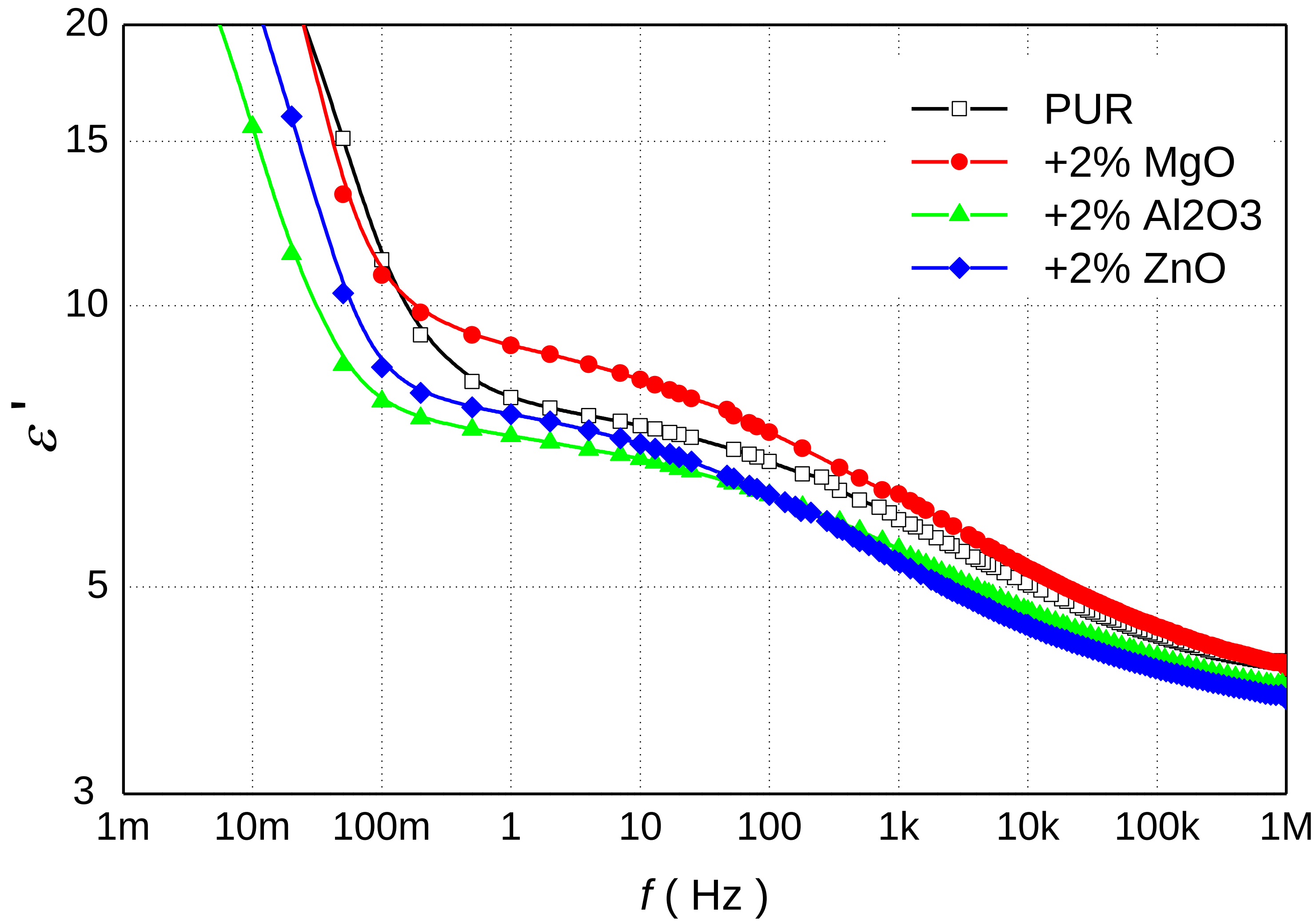


The frequency dependence of thdisipation factor (b) for *polyeurethan* with various concentrations of MgO nanoparticles.

Type	PUR	+0.5% MgO	+1% MgO	+2% MgO
$\Delta\varepsilon_1$	3,85	3,82	3,43	5,86
ε_∞	3,92	2,82	3,13	3,69
τ_1 (μs)	0.13	0,93	0,713	0,351
f_{01}(Hz)	7,8k	1,17k	1,4k	2,85k
α_1	0,41	0,30	0,41	0,31
σ (10^{-12})	14,3	24,9	44,5	16,2
$\Delta\varepsilon_2$	25,6	10,02	24,3	11,48
τ_2 (s)	6,37	1,29	1,37	15
f_{02} (Hz)	0.16	0,77	0,73	0,06
α_2	0,21	0,04	0,13	0,13

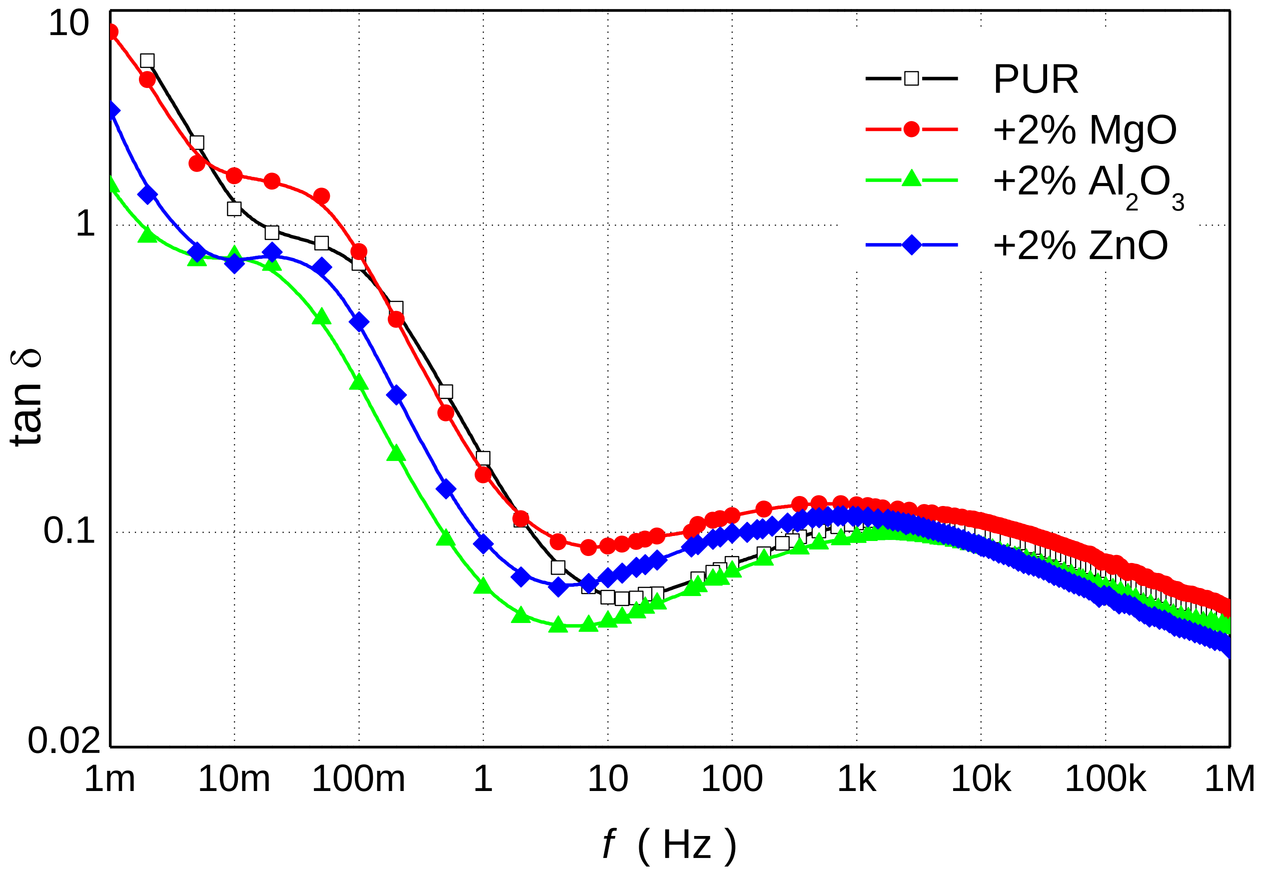
PARAMETERS OF THE COLE-COLE MODEL FOR POLYEURETHAN AND ITS MIXTURE WITH MGO TEMPERATURE 60° C.

Different type of nanoparticles



The frequency dependence of the real part of the complex relative permittivity for the polyeurethan with 2.0 wt% various nanoparticles at 60 °C.

Different type of nanoparticles



Type	PUR	+2% Al_2O_3	+2% MgO	+2% ZnO
$\Delta\varepsilon_1$	3.85	3.9	5.9	4.1
ε_∞	3.9	3.6	3.7	3.7
τ_1 (μs)	**128**	**220**	**350**	**390**
f_{01}(Hz)	**1240**	**718**	**454**	**411**
α_1	0.6	0.63	0,69	0.61
σ	14.2	1.9	16,1	4.37
$\Delta\varepsilon_2$	25.6	23.1	48.3	29.2
τ_2 (s)	**6.37**	**24.8**	**15.9**	**15.9**
f_{02} (mHz)	**25**	**6**	**10**	**10**
α_2	0.21	0.12	0.12	0.11

6. Conclusion

- The dielectric spectroscopy were used for the study of the polyeurethan and its mixture of MgO, ZnO and Al_2O_3 nanoparticles.
- The complex permittivity measured within the frequency range from 1 mHz to 1 MHz was dependent on the temperature.
- The decrease of the real permittivity was caused by the presence of highly immobile polyeurethan in the interfacial regions around nanoparticles.
- α- and IDE-relaxation processes were observed.
- The shift of peak related to the α-relaxation process to higher frequencies caused by nanoparticles was observed.