Dielectric liquids, history, diagnostic and issue of nanofluids

Visegrad Fund

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ViF- Engineering platform and cooperation for analysis of nanocomposites

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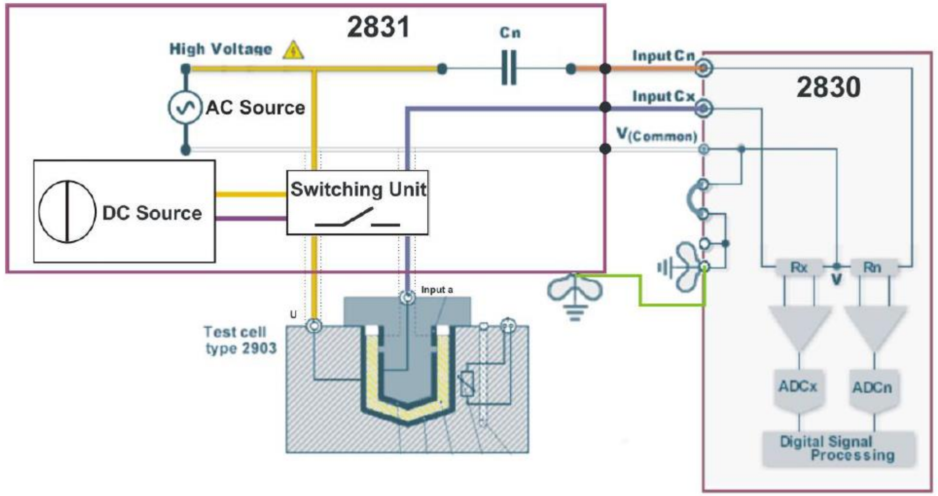
www.fel.zcu.cz

Introduction

Dielectric liquids

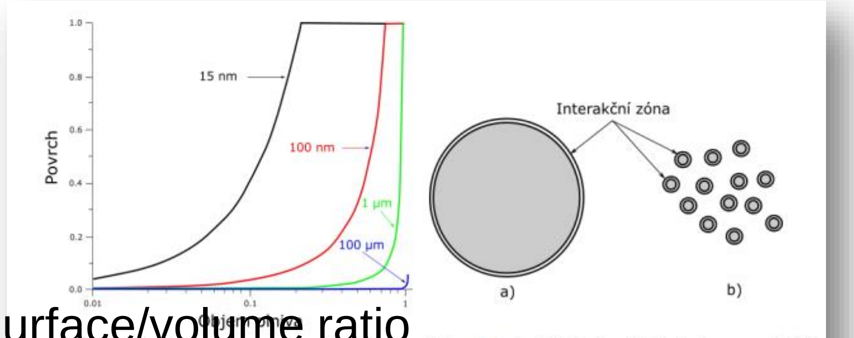
- Dielectric liquids are an inseparable part of various electrical appliances and machines. They are used in cables, switches, capacitors, and transformers. The presentation covers a brief history of using dielectric liquids, diagnostic methods used for dielectric liquids, searching for new liquids proper for the environment, and sustainable development. Addressed will be the problems with material compatibility, different physical properties of new liquids, and new **nanofluids**.



Content

Dielectric Liquids

- Introduction of the FEE UWB
- Short history of using DL
- Our research in the field
- Selected oil parameters & related oil diagnostics
- Biodegradable nanofluids based on ENVITRAFOL



Surface/volume ratio

Obr. 4: Poměr povrchu rozhraní / objemu plniva (*převzato z [14]*)

Obr. 5: Interakční zóna částic (*převzato z [13]*)

[13] KOCHETOV, R. Thermal and Electrical Properties of Nanocomposites, Including Material Processing. Finland, 2012. Disertační práce. Lappeenranta University of Technology.

University of West Bohemia

City	Pilsen (CZ)
Founded in year	1991 (1950)
Number of employees	2132
Number of students	14 500
Annual sales	77 million €
Core business	University, Research institute
FACULTIES AT THE UNIVERSITY	
Faculty of Applied Sciences	
Faculty of Economics	
Faculty of Electrical Engineering (FEE)	
Faculty of Philosophy and Arts	
Faculty of Education	
Faculty of Law	
Faculty of Mechanical Engineering	
Faculty of Health Care Studies	
Faculty of Art and Design	

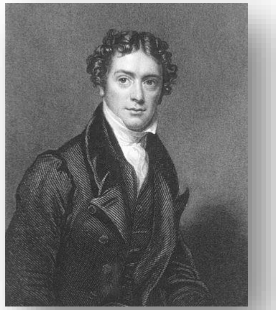
R&D center RICE

Basic Overview - Research and Innovation Centre for Electrical Engineering

- **RICE** is a trademark of the Faculty of Electrical Engineering in Pilsen, **Czech Republic** for the R&D area.
- **Close to 200 researchers.**
- **Whole research chain** from basic (theoretical) research up to development of functional samples and their complete testing.
- R&D projects with **total budget approaching 100 mil. EUR**.
- **Leader / coordinator of more than 70% of the projects.**

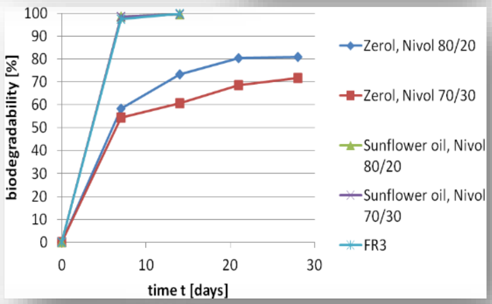
High Voltage Electric Insulation Materials

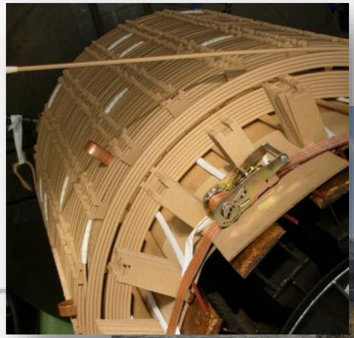
TRANSFORMER'S INSULATION HISTORY		
EIS	**From**	**Observation**
Commercial Oil Extraction (Romania)	1857	Than Bulgaria and USA
Petroleum based oil use in transformer	1887	For transformer cooling
Oil–insulated transformer (Brown). The oil cellulose two-phase insulation system	1890	**Way to high power and high voltage**
3 phase HV transformers with mineral oil (AEG)	1890, 1891	Evidence of the benefits of HV for energy transfer



Dielectric fluids used in transformers - overview

Paraffinic oils	1890 - 1925	Pour point
Naphthenic oils	1925-1930	Health issues
PCB (Ancolor, Delor), not flammable	1932 – 1978	CZE e.g. till 1986
Silicon/Kraft Paper later Silicon/Aramide Paper	1970	PCB replacement
Synthetic Esters, e.g. MIDEL 7131 – less flammable for lower voltage -rolling stock transformers	1980	Biodegradable
Natural esters	2004	Sustainable development, higher thermal class and fire point
Nanofluids with mineral, natural ester	2008/2012	BDV increase
GTL, NITRO BIO	2020	Shell Qatar 2011





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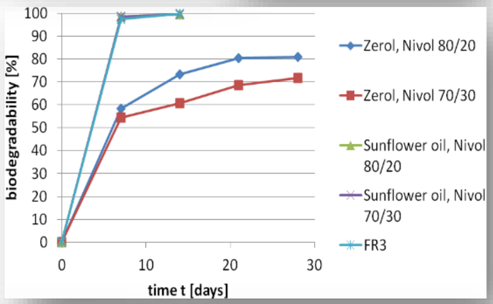
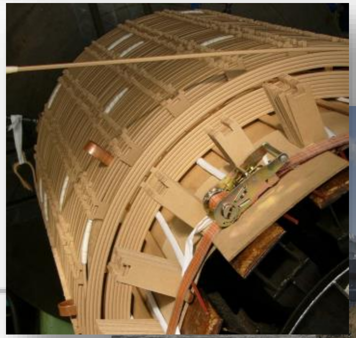
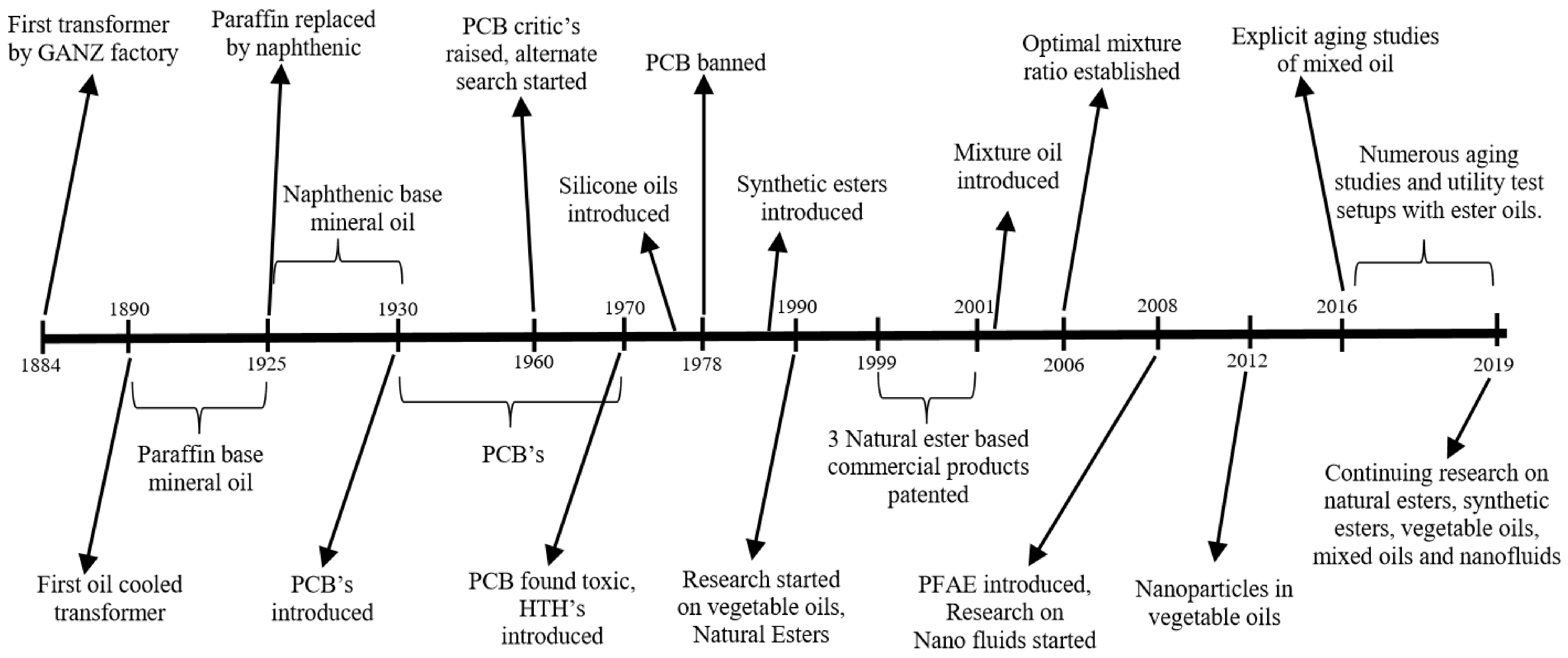
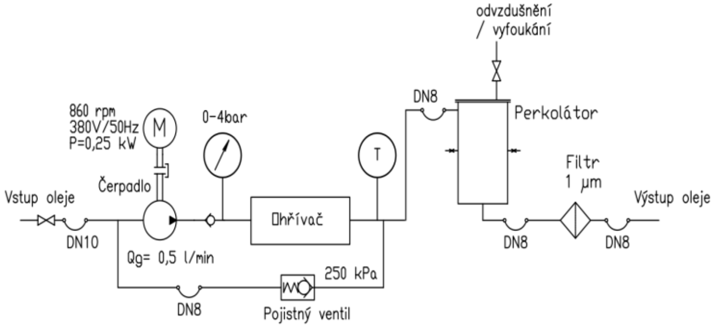


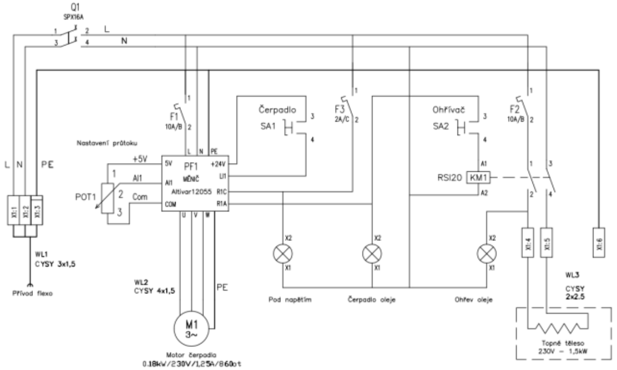




Alternative Dielectric Fluids for Transformer Insulation System: Research Progress, Challenges, and Future Scope

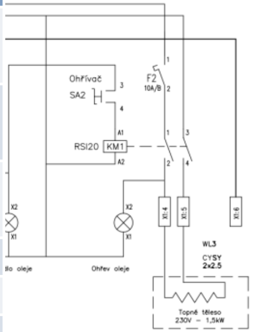
Developing of biodegradable fluid





Developing of biodegradable fluid

Parameter (Unit)	Limit Value from IEC 62770	ENVITRAFOL
Before Test of Oxidative Stability		
Appearance	Clear, free of sediment and suspension	Fulfill
Viscosity at 100 °C (mm^2/s)	max 15	8.26
Viscosity at 40 °C (mm^2/s)	max 50	35.84
Pour point (°C)	max -10	-24
Water content (mg/g)	max 200	45.8
Density at 20 °C (g/ml)	1.0	0.915
Breakdown voltage (kV/2.5 mm)	min 35	60
Dissipation factor at 90 °C (-)	max 0.05	0.00358
Acid number (mgKOH/g)	max 0.06	0.011
Corrosive sulfur / DBDS	absent / below the limit of determination	absent
Additives antioxidants DBCP (wt %)	max 5	0.53
Additives all (wt %)	max 5	DBPC only
After Test of Oxidative Stability		
Dissipation factor at 90 °C (-)	max 0.5	0.02157
Viscosity at 40 °C (mm^2/s)	maximum increase of previous value of 30%	35.3
Acid number (mgKOH/g)	max 0.6	0.041



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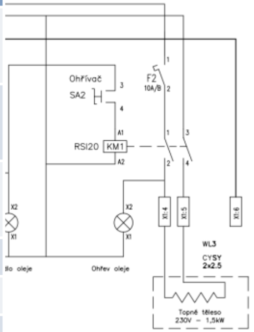
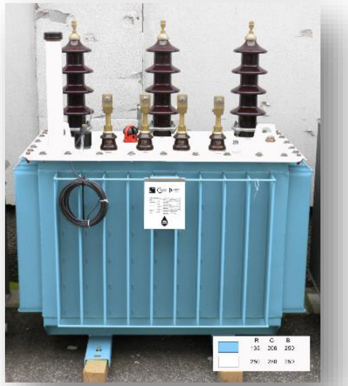


Continuing of the development

Biodegradable electrical insulating fluid ENVITRAFOL	UV CZ 29 982 U1 Biodegradable electrical insulating liquidTK02020017 - INBIO TA 03020251 Insulating liquids
Compliance with the normative requirements	BDV, Acid Number, tan δ, ρ_v, oxidation stability, water content
Parameters of EIS	Temperature stability, oxidative stability, E_p, ρ_v, tan δ, Low temperature properties
Compatibility test	All components of the transformer
Setting the diagnostic values	For diagnostics in operation
Parameter improvement, nanofluids	Reduction of water content, E_p, ρ_v, viskosity, 0.25 wt% TiO_2, inhibitors
Research in the field of Partial Discharges	Different electron mobility, different streamer length
EU Ecodesign II requirements	Regulation (EU) 2019/1783 , P_{0max} < 189 W



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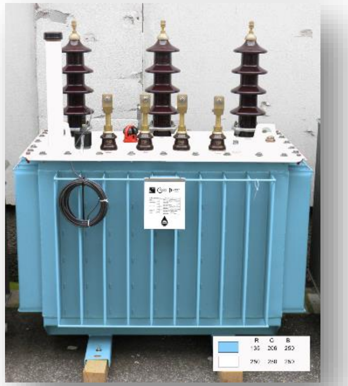
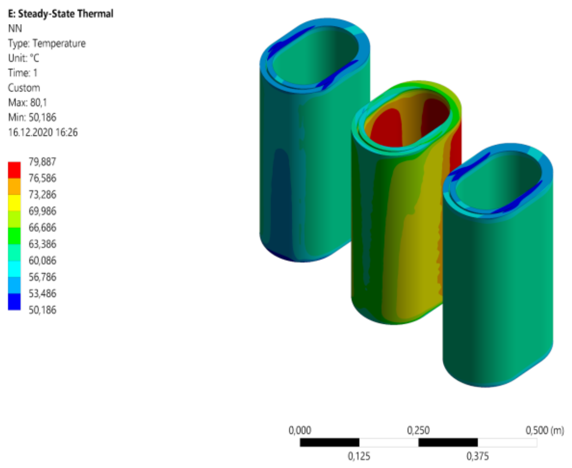
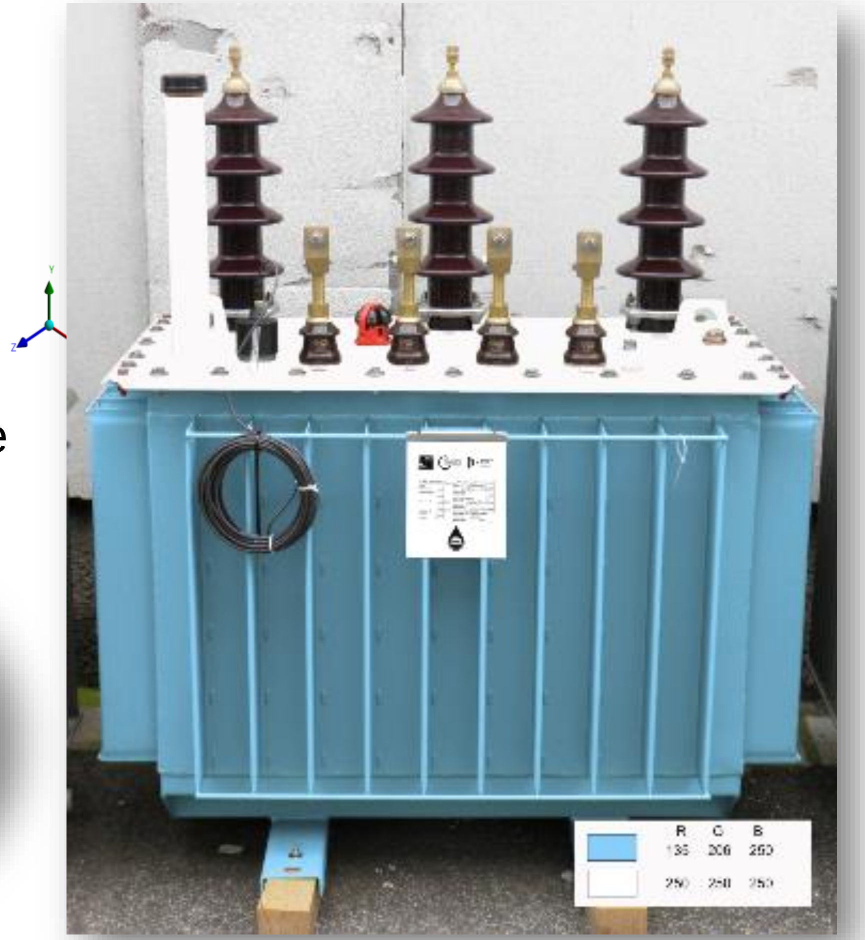
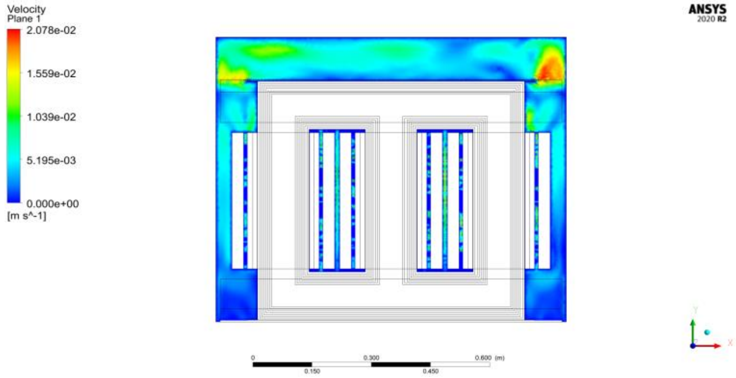


Distribution transformer with ENVITRAFOL

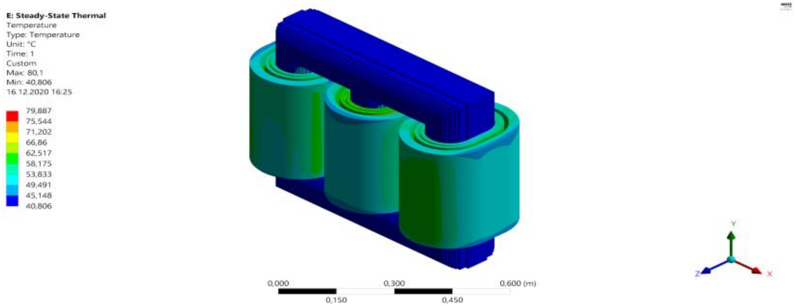


Temperature over low voltage winding



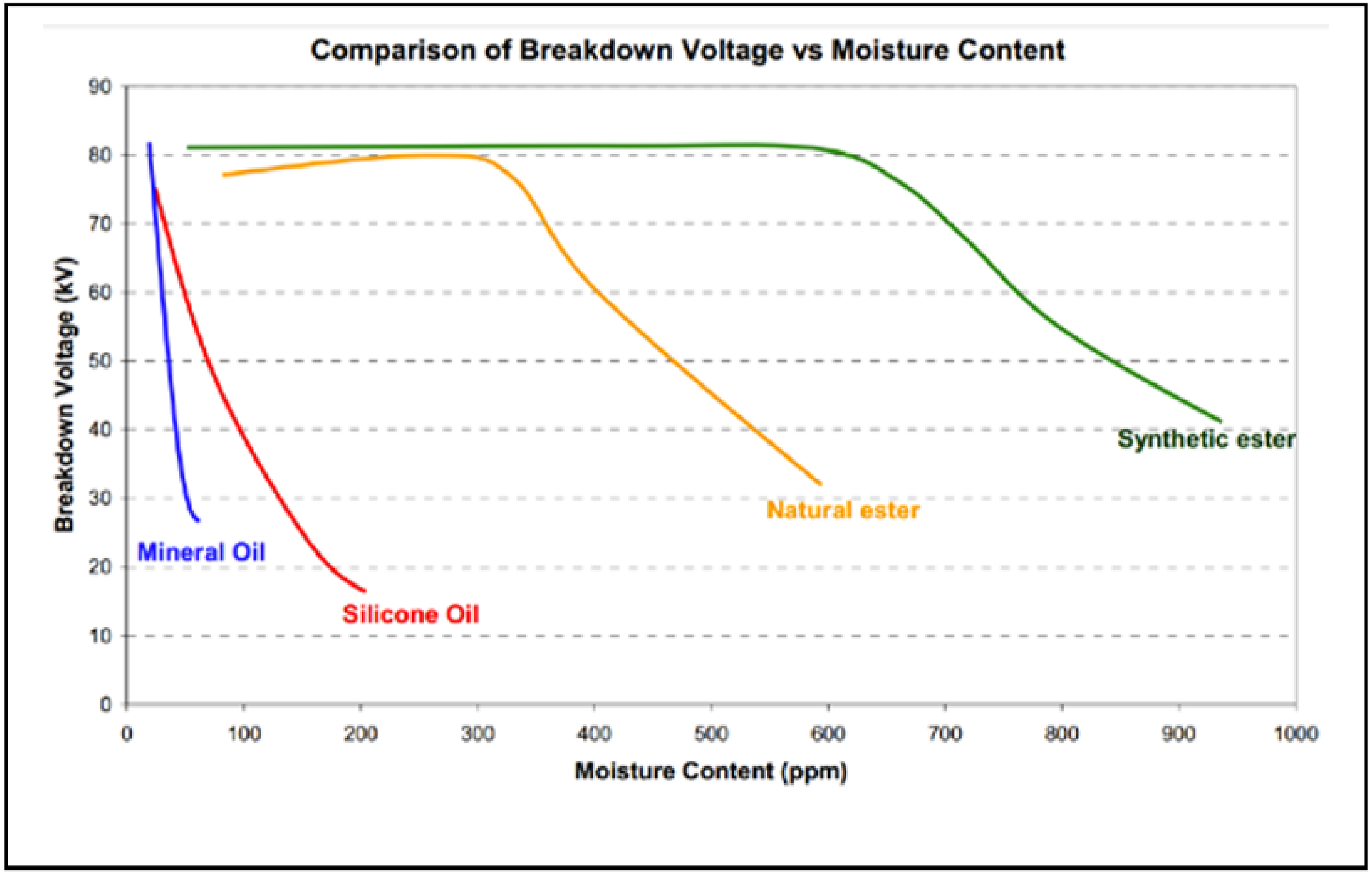


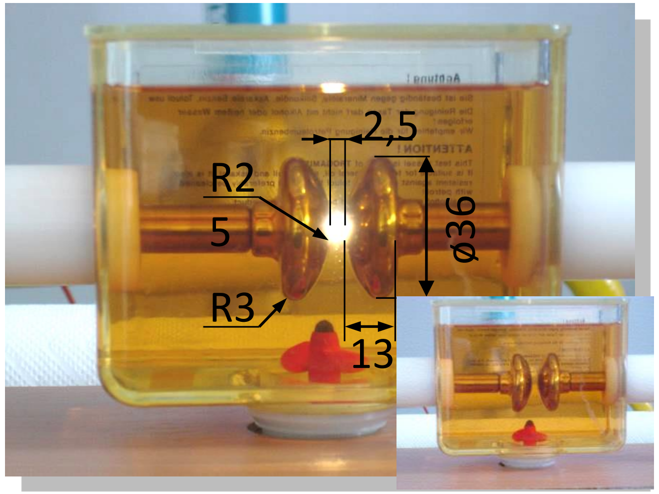
Oil flow

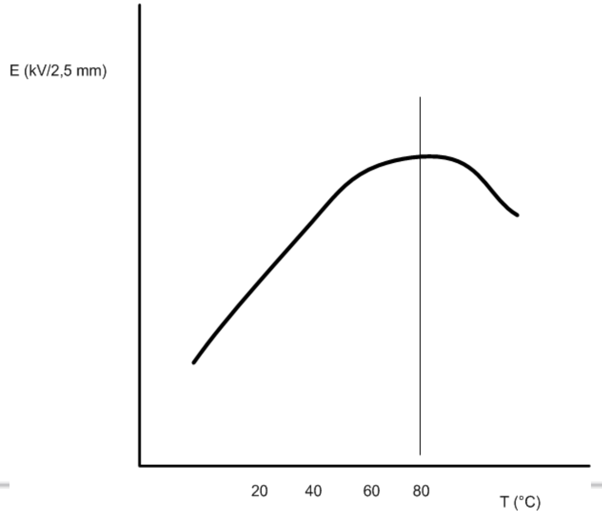


Selected properties of ester fluids

Breakdown Voltage

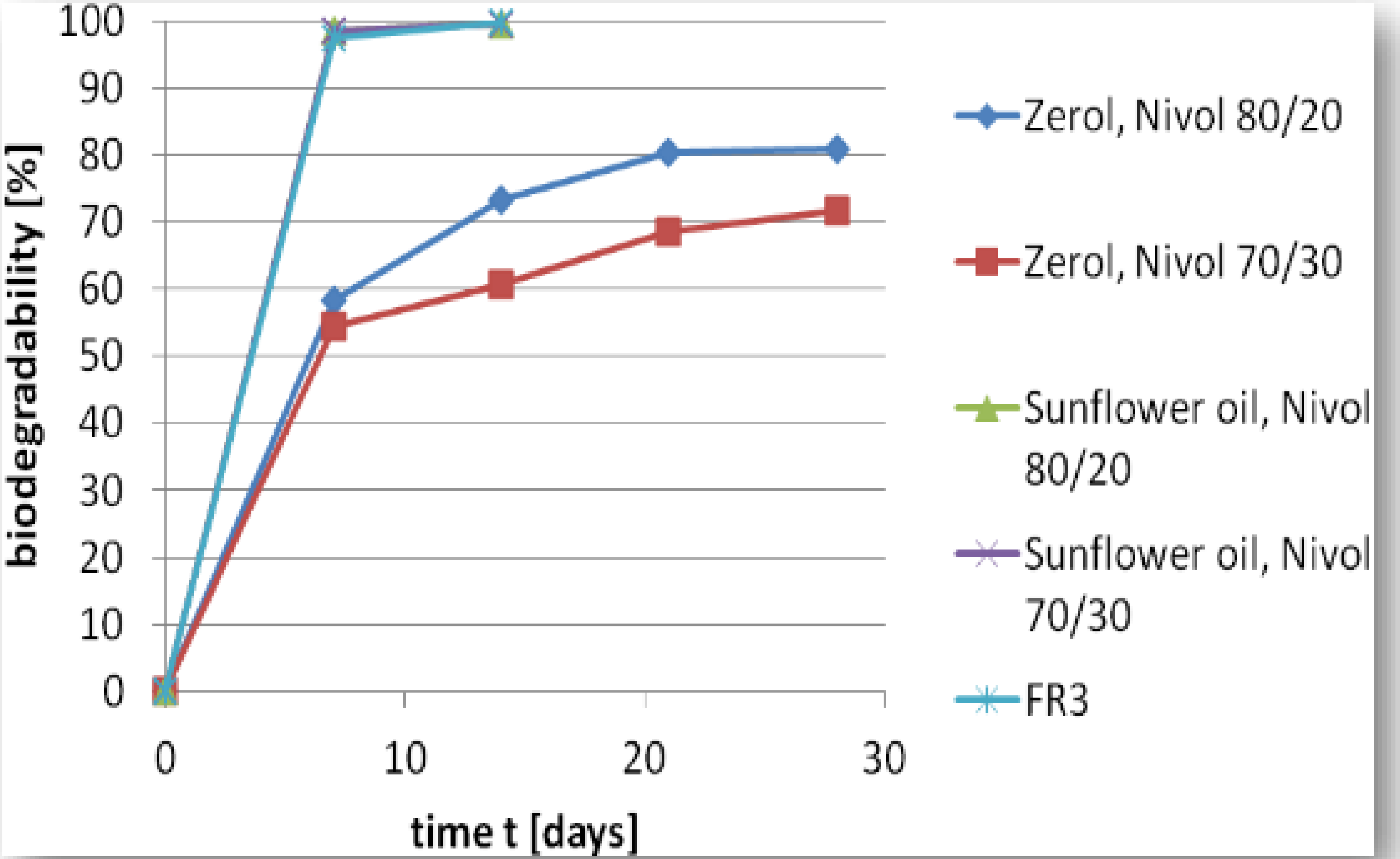






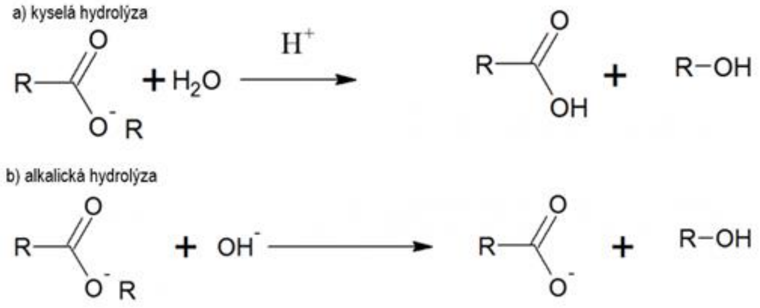
Some properties of ester fluids

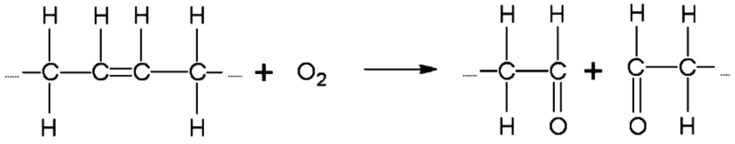
Biodegradability OECD 301

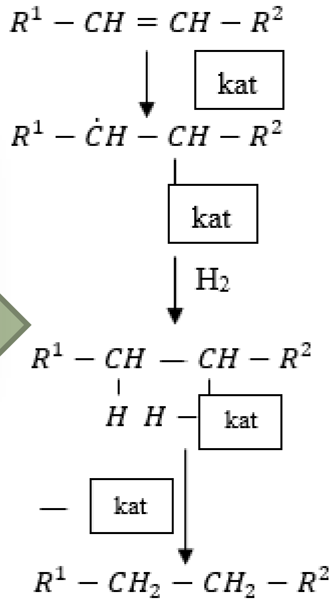


Changes in the Ester Oils - aging

Hydrolysis
Oxidation Of Natural Esters (unsaturated and > 100°C saturated as well
Polymerization The degree of oxidation depends on the content of carbon double bonds C = C - weak points
Hydrogenation



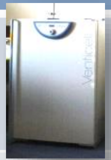
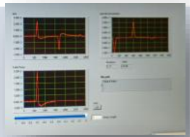
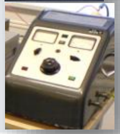
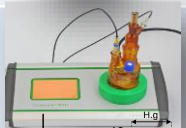
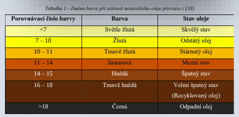
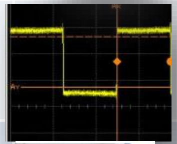
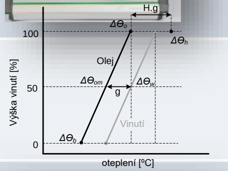
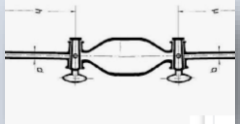
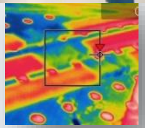
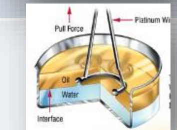




Saturated f.a = better oxidation stability **X** higher viscosity
Unsaturated m. = worse oxidative stability **X** lower viscosity

Conflicting properties - Pour point

Diagnostics methods for insulating fluids

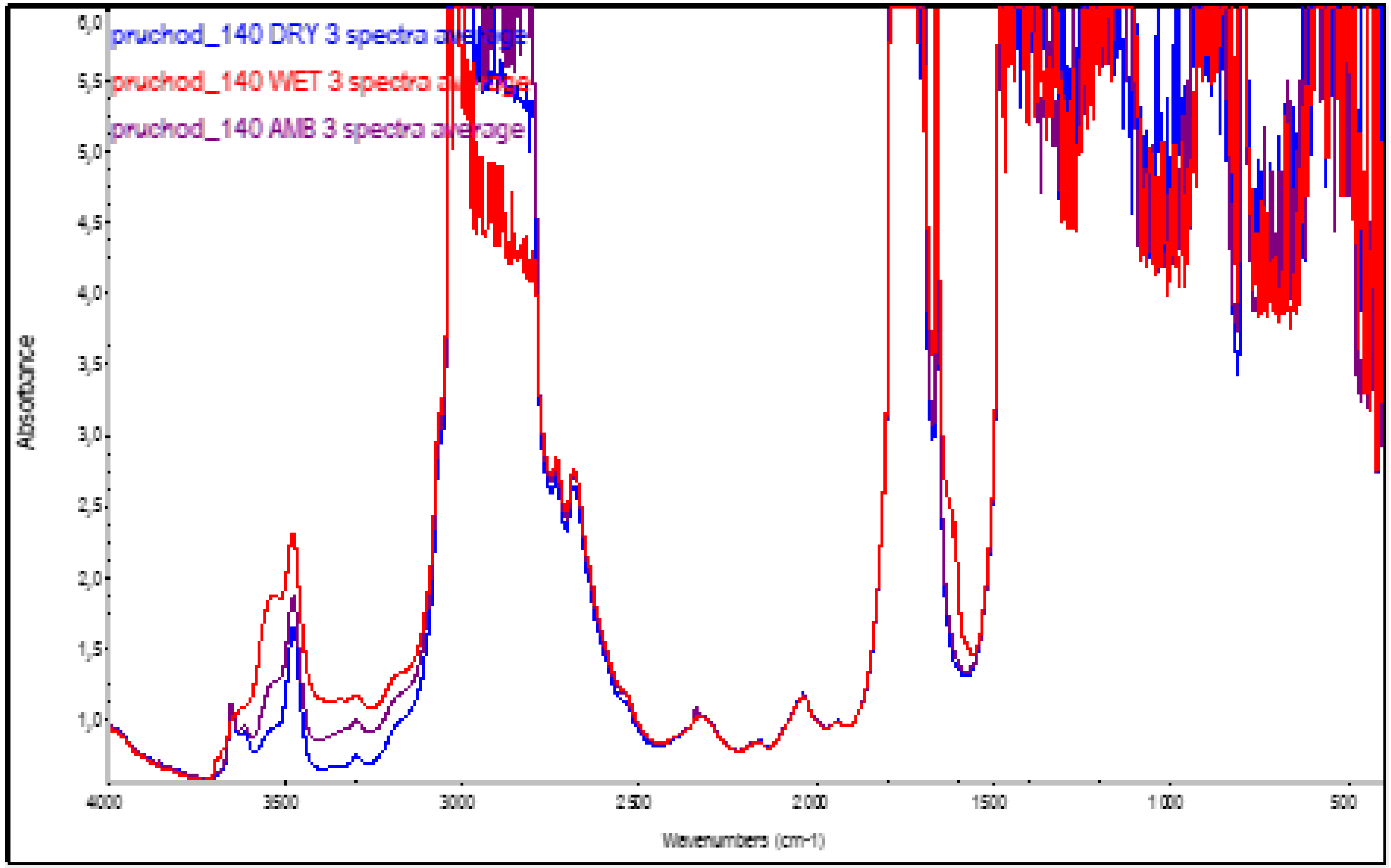
Aging		Electric		Non-electric		Optical	
Thermal		Space Charge		Viscosity, Density		Microscopy	
Electric HVDC		BDV		Acid number		Corrosive Sulphur	
Electric HVAC		Tan $\delta = f(U, T, f)$		Water cont.		Color	
Pulse voltage		ρ_v, R_{iz}, p_{i1}		Hot-Spot		FT IR Inhibitor cont.	
Climatic		PD		Gas cont.		UV	
Oxidation stability		ε', ε'' =f(f, T)		Fire point		IR	
Compatibility				Pour point		Monitoring	
				Interfacial tension		Visual	

Tabulka 1 - Změna barvy při stárnutí minerálního oleje převzato z [33]

Porovnávací číslo barvy	Barva	Stav oleje
<7	Světle žlutá	Skvělý stav
7 – 10	Žlutá	Odstátý olej
10 – 11	Tmavě žlutá	Stárnutý olej
11 – 14	Jantarová	Mezní stav
14 – 15	Hnědá	Špatný stav
16 – 18	Tmavě hnědá	Velmi špatný stav (Recyklovaný olej)
>18	Černá	Odpadní olej

FTIR Example

Natural ester aged by Temperature (with paper, moisture and Copper)



Source:RICE

FTIR Example

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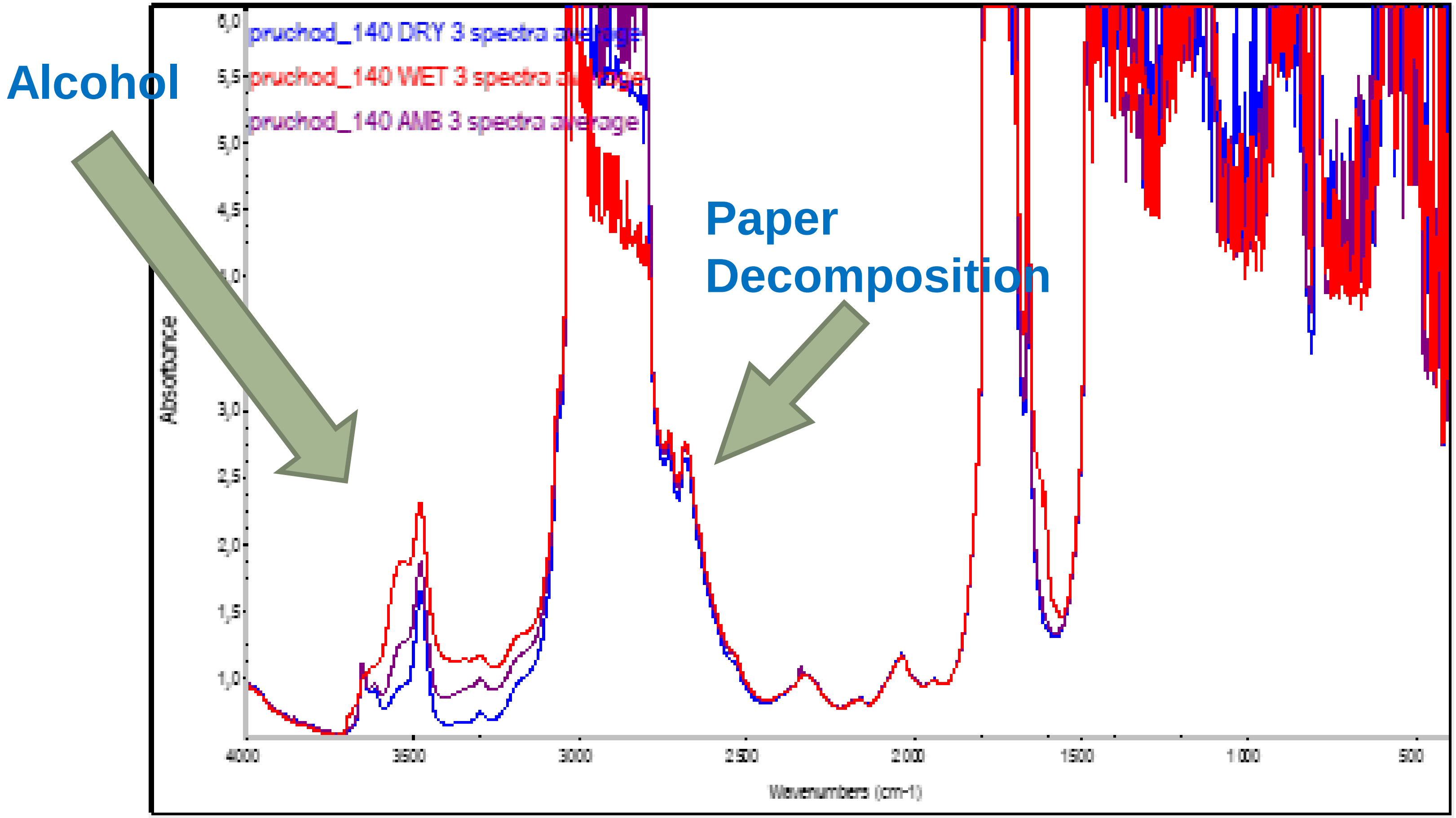
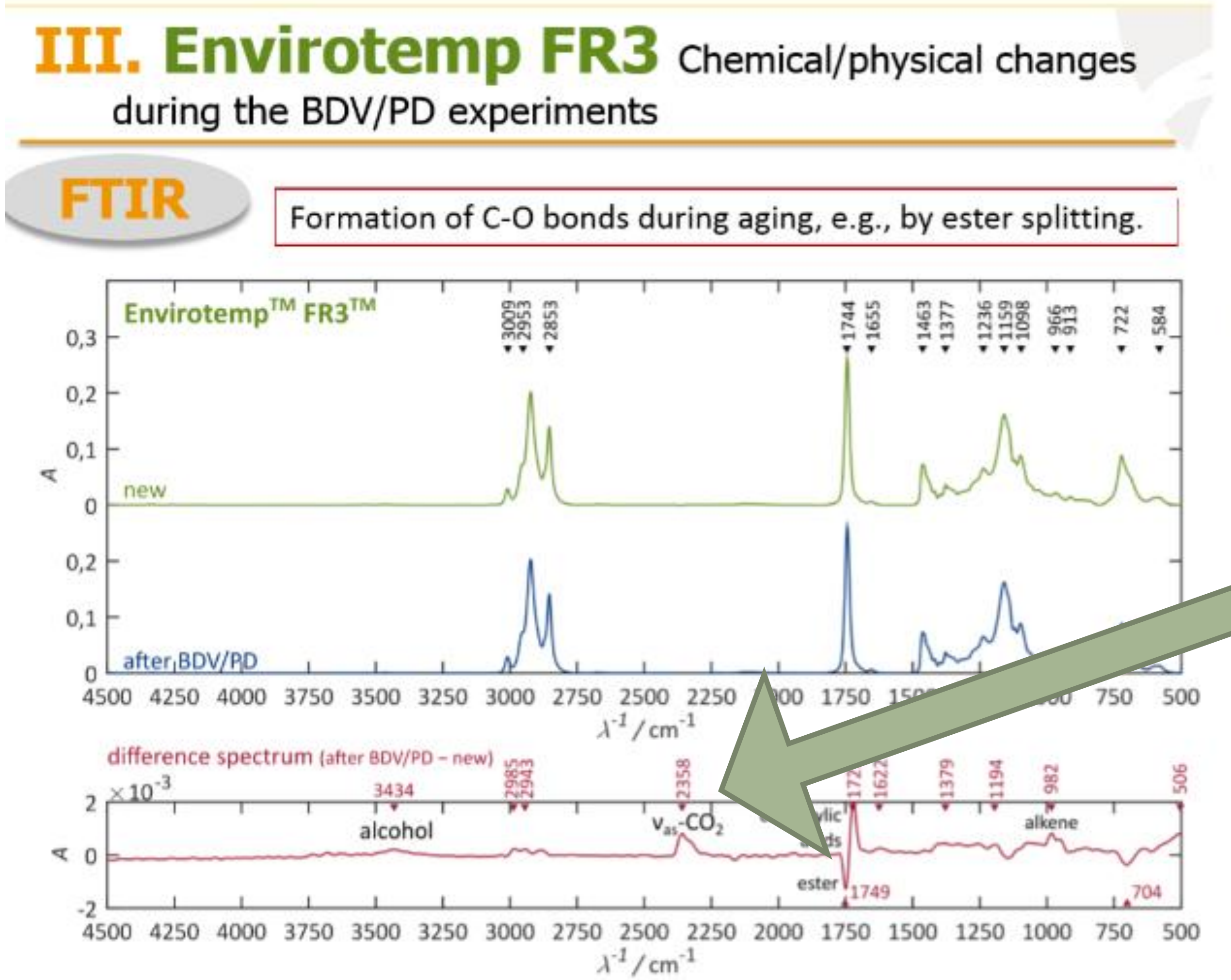


Source:RICE

FTIR Example

Natural Ester Aged by Impulses



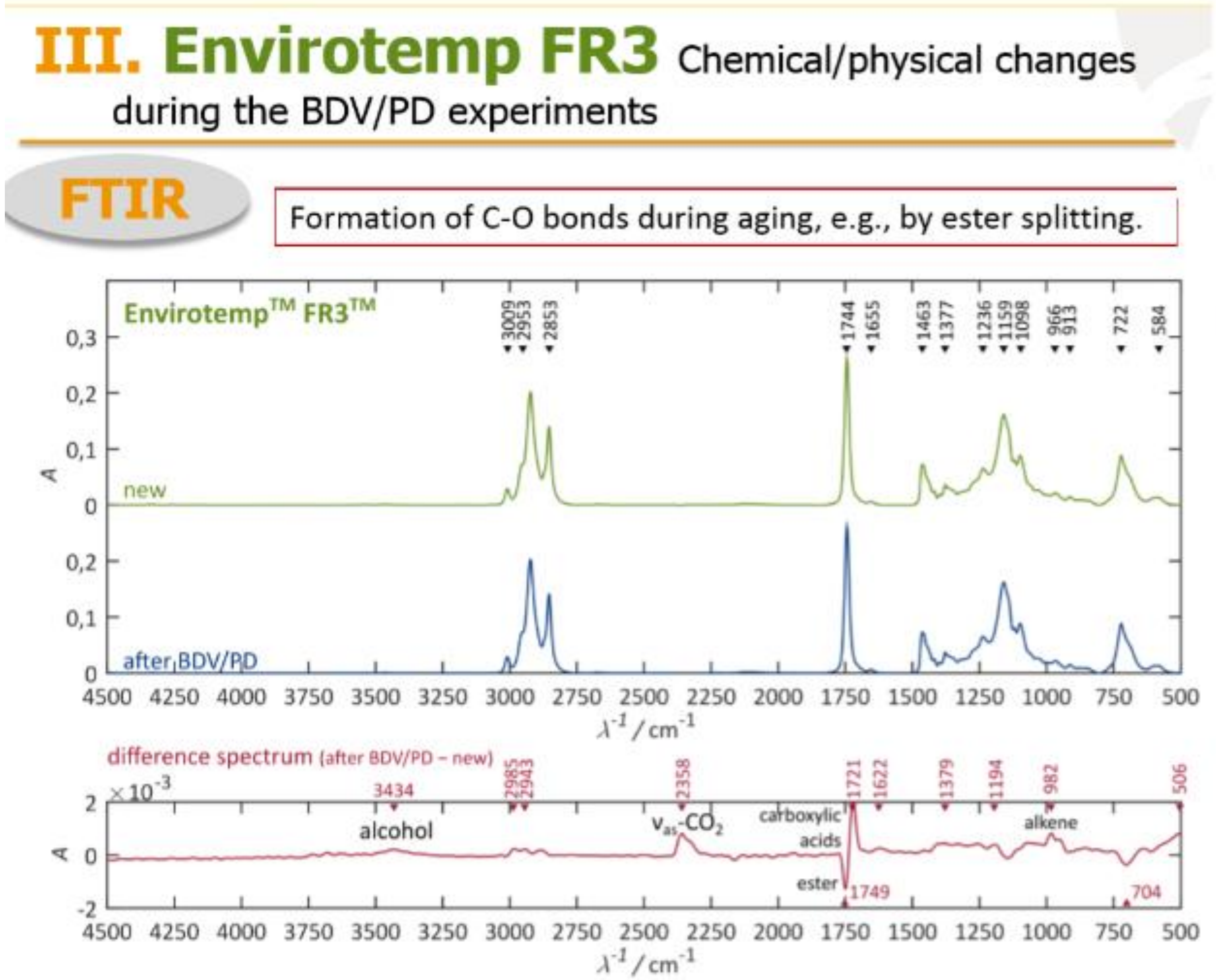
Impulses and BDV

Source: UMTRIS

FAKULTA ELEKTROTECHNICKÁ
ZÁPADOČESKÉ UNIVERZITY
V PLZNI

FTIR Example

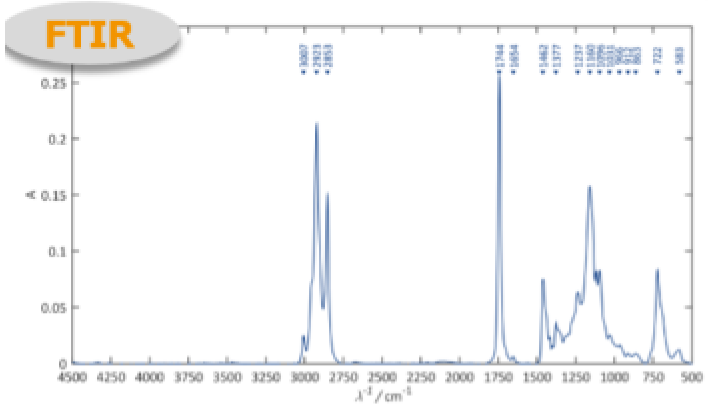
Natural Ester Aged by Impulses

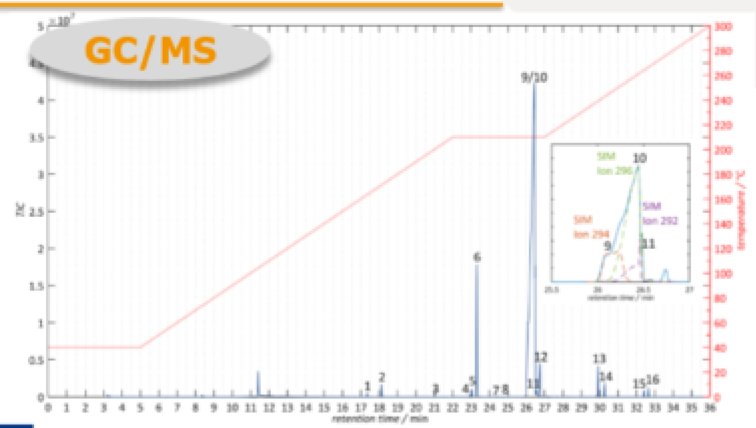


Source: UMTRIS

GC/MS

IV. ENVITRAFOL structural analysis

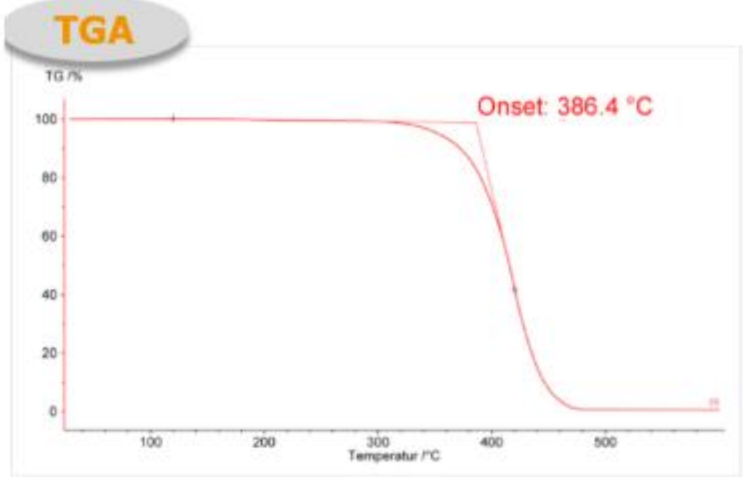


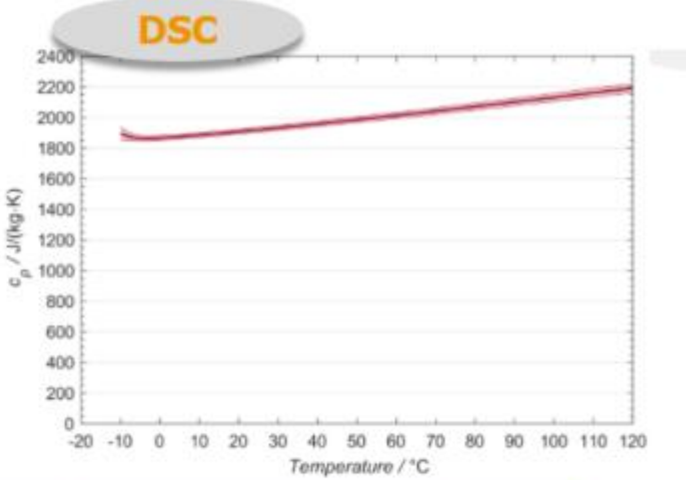


#	RT min	Peak-A %		Qual %
3	21.05	0.06	Tetradecanoic acid, methyl ester (Myristic acid, methyl ester)	99
4	22.92	0.05	7,10-Hexadecadienoic acid, methyl ester	99
5	23.04	045	9-Hexadecenoic acid, methyl ester,(Z)- (Palmitoleic acid, methyl ester)	99
6	23.30	6.03	Hexadecanoic acid, methyl ester (Palmitic acid, methyl ester)	99
7	24.40	0.08	cis-10-Heptadecenoic acid, methyl ester	99
8	24,76	0,05	Heptadecanoic acid, methyl ester (Margaric acid methyl ester)	98
9	26.22	19.2	9,12-Octadecadienoic acid (Z,Z)-, methyl ester (Linoleic acid, methyl ester)	
10	26.45	57.9	9-Octadecenoic acid (Z)-, methyl ester (Oleic acid, methyl ester)	
11	26.57	10.1	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)- (Linolenic acid, methyl ester)	96
12	26.75	2.16	Octadecanoic acid, methyl ester (Stearic acid, methyl ester)	99
13	29.92	1.80	cis-11-Eicosenoic acid, methyl ester	99
14	30.27	0.68	Eicosanoic acid, methyl ester (Arachidic acid methyl ester)	99
15	32.41	0.36	13-Docosenoic acid, methyl ester,(Z)- (Erucic acid methyl ester)	98
16	32.37	0.37	Docosanoic acid, methyl ester (Behenic acid, methyl ester)	99

Source: UMTRIS

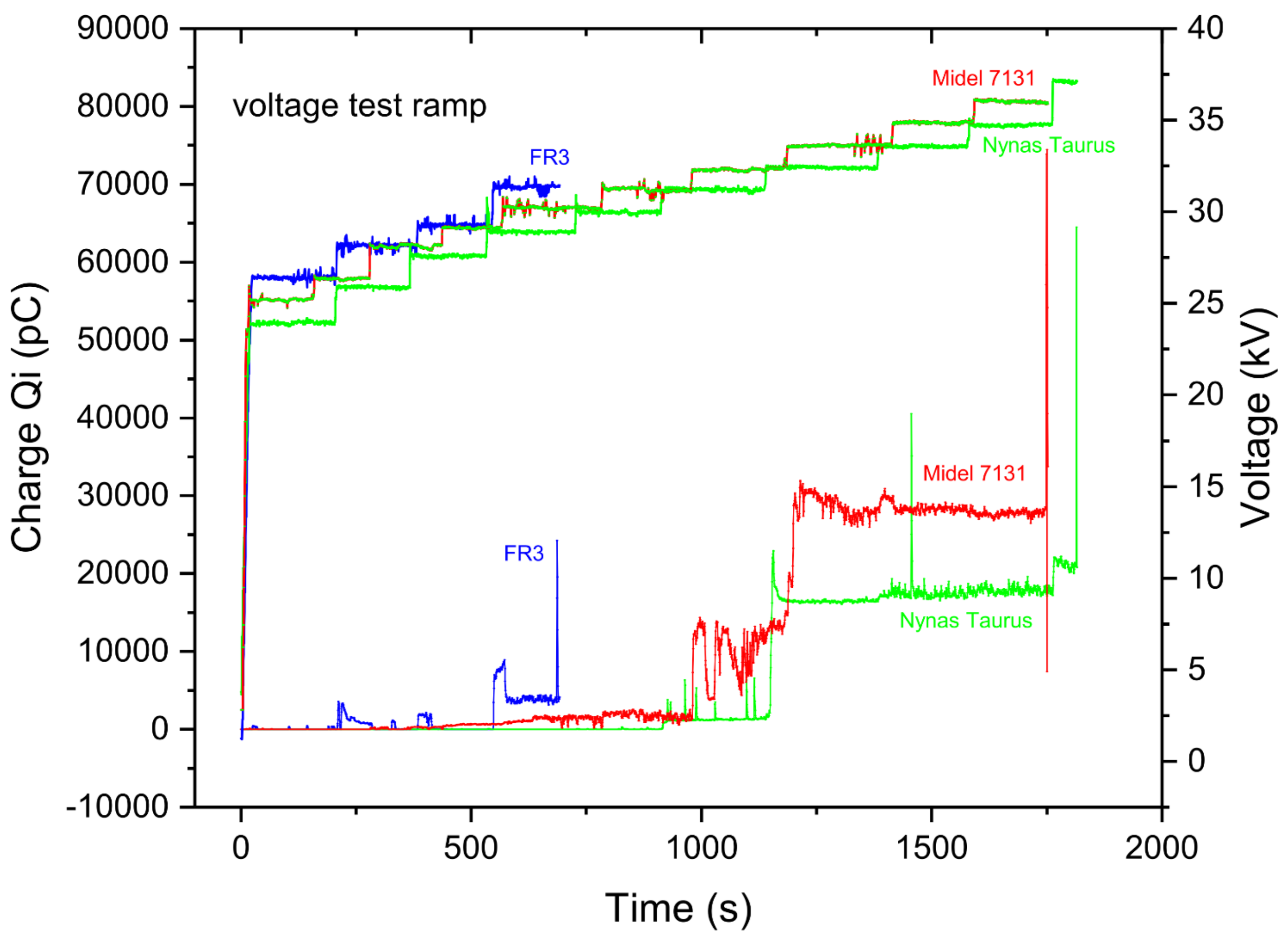
IV. ENVITRAFOL physical/chemical parameters



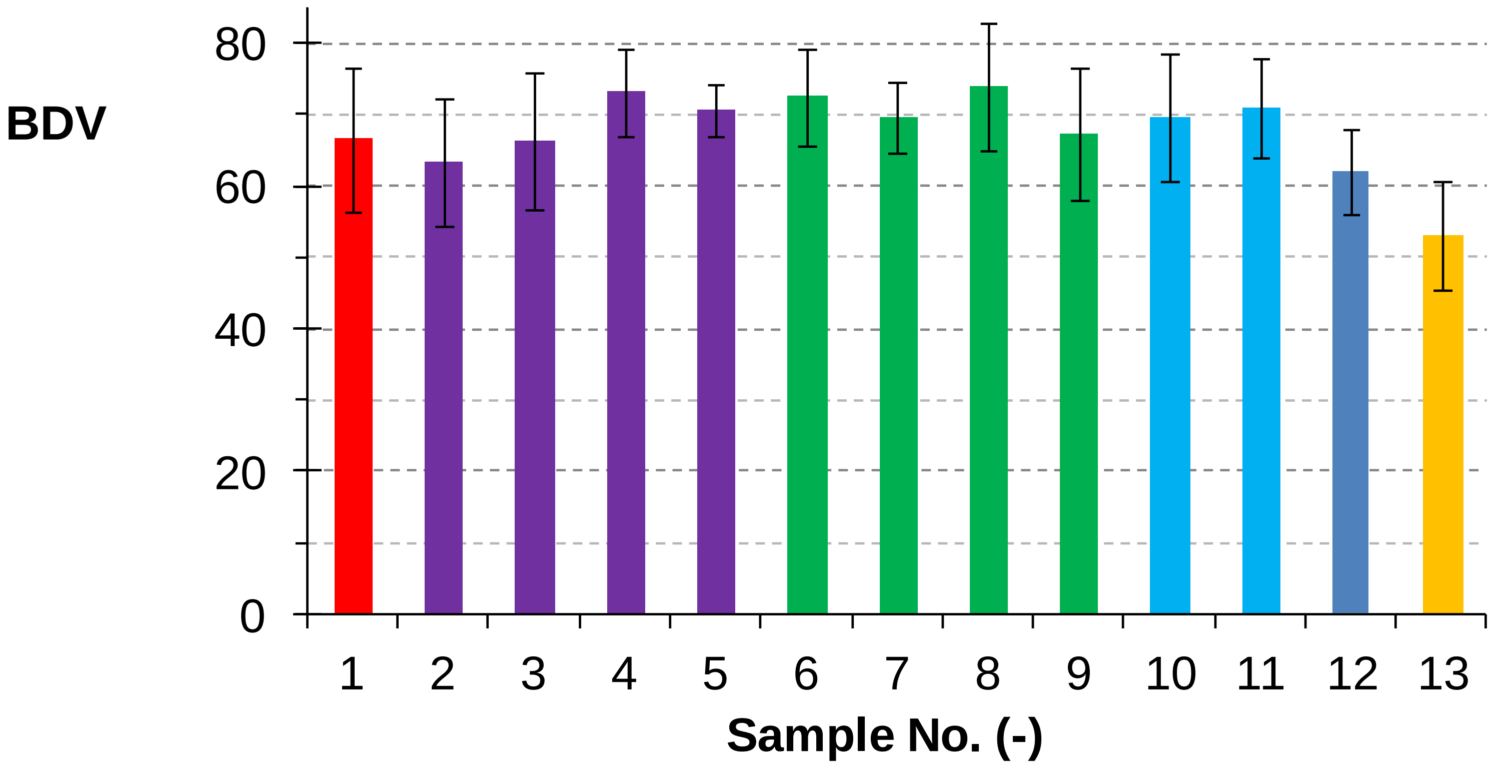


ENVITRAFOL		BDV/PD	Unit
Water content		319.94 ± 4.80	mg/kg
Density (20°C)	ρ	0.9156 ± 0.0007	g/cm³
Density (40°C)	ρ	0.9064 ± 0.0012	g/cm³
Specific heat capacity (60°C)	c_p	1998 ± 20	J/(
Relative premittivity (20°C; 1kHz)	ε_r	3.031	
Dissipation factor (80°C; 1kHz)	tan δ	0.009	
Decomposition temperature	T	386.4	°C

Different PD Behavior



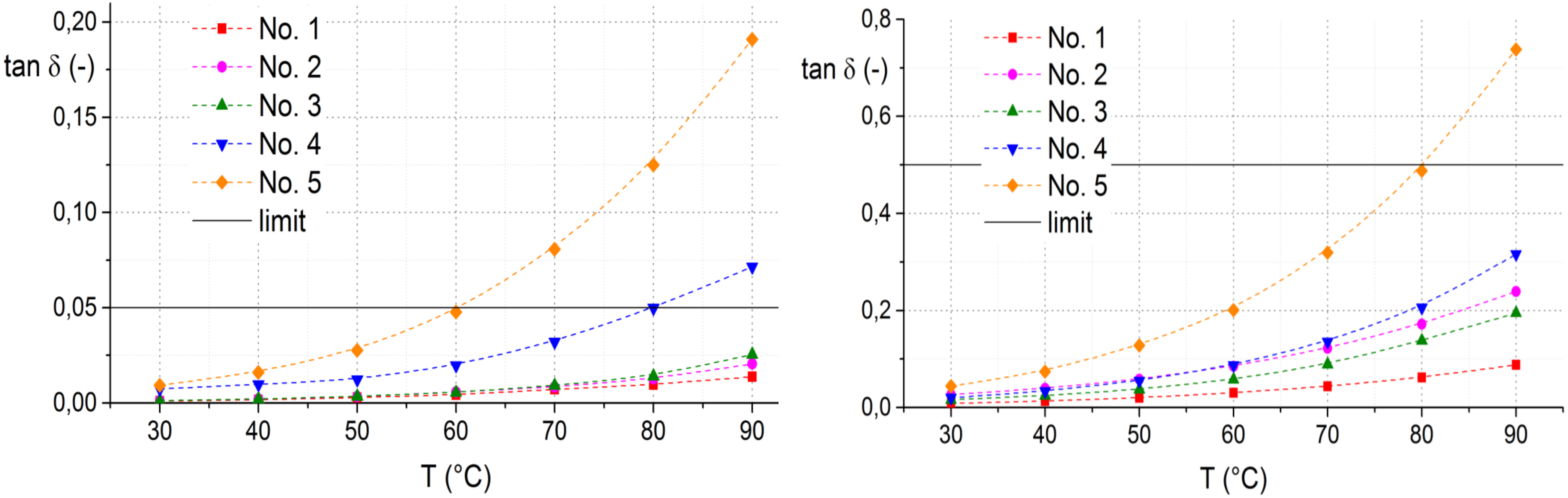
BDV vs Different Antioxidants



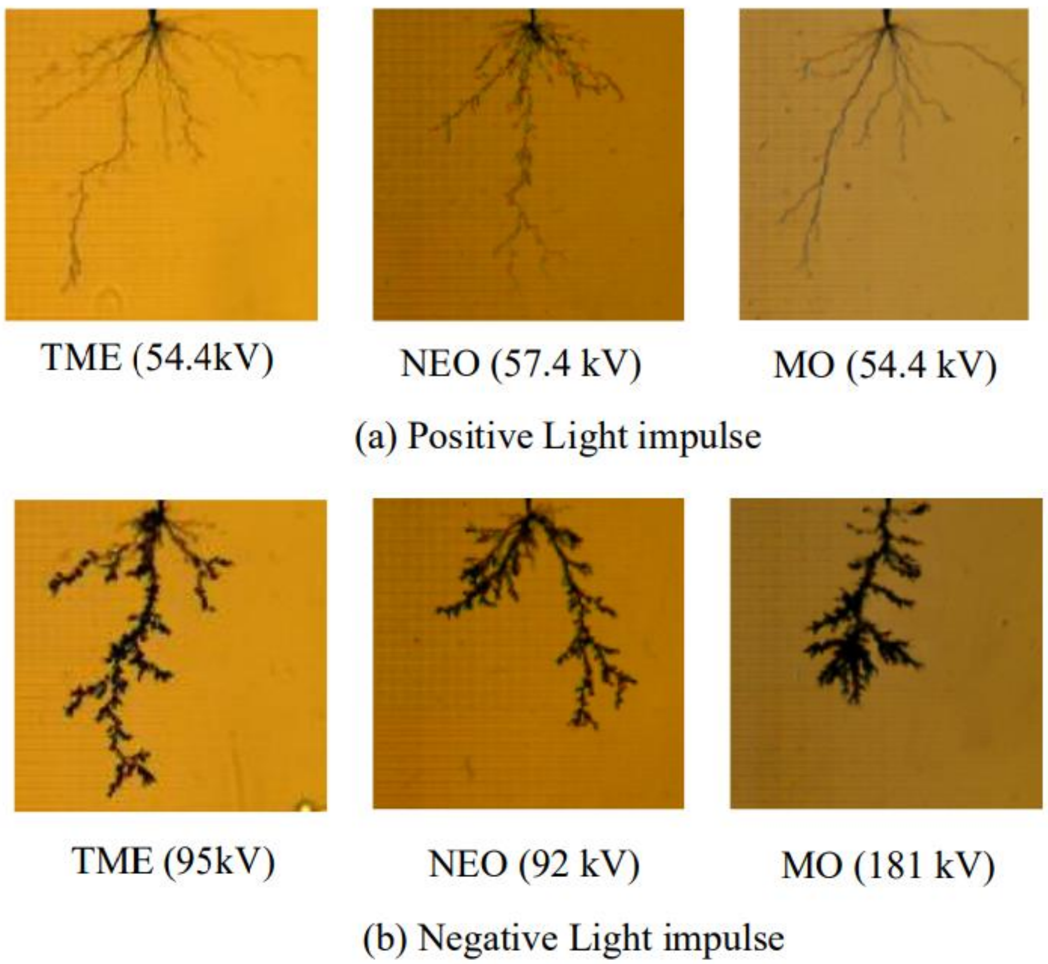
Tab. 7: Označení vzorků s antioxidanty

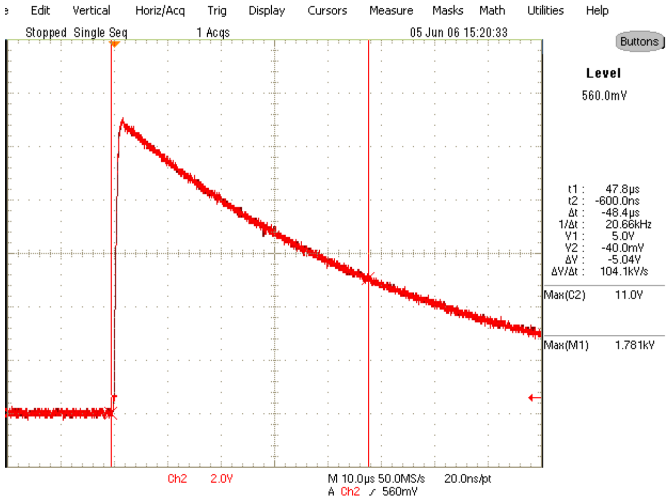
Antioxidant	Označení vzorku				
PG	Číslo	2	3	4	5
	Množství [$\%_{hm}$]	0.05	0.1	0.25	1
BTHQ	Číslo	6	7	8	9
	Množství [$\%_{hm}$]	0.1	0.25	0.5	1
PG s CA	Číslo	10		11	
	Množství [$\%_{hm}$]	0.1 + 0.1		0.25 + 0.25	
BTHX	Číslo	12			
	Množství [$\%_{hm}$]	1			
CA	Číslo	13			
	Množství [$\%_{hm}$]	1			

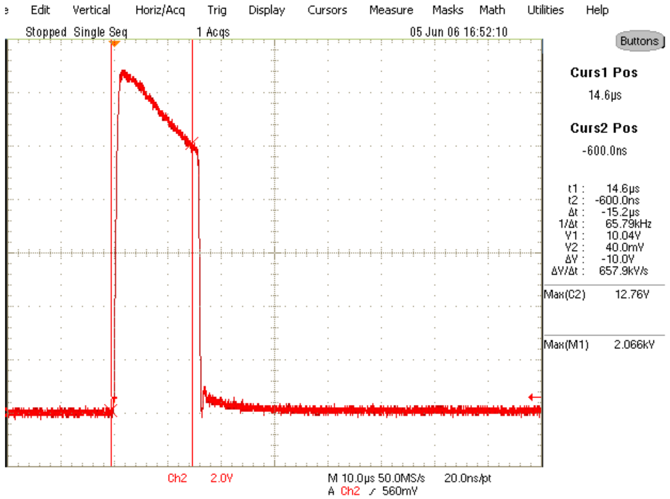
Dissipation factor before and after TOS vs Antioxidant



LI streamers in various oils





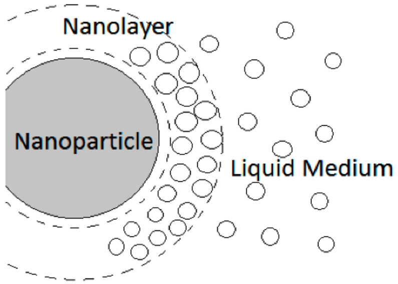


- Trimetil ester, New ester, Mineral oil, pictures of streamers LI

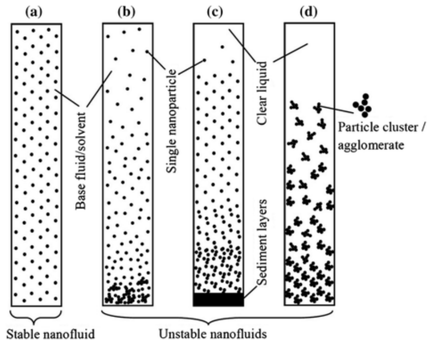
Nanofluids

Dielectric nanofluids

- Dielectric **nanofluid** is a fluid containing nanometer-sized particles, usually in the form of colloidal suspensions of nanoparticles in a base fluid. The nanoparticles used in dielectric nanofluids are typically oxides (TiO_2, SiO_2, CuO, ZnO, MgO and Al_2O_3).



https://www.mdpi.com/2076-3417/9/1/87



https://link.springer.com/chapter/10.1007/978-3-319-29761-3_1

Nanofluid with Envitrafol

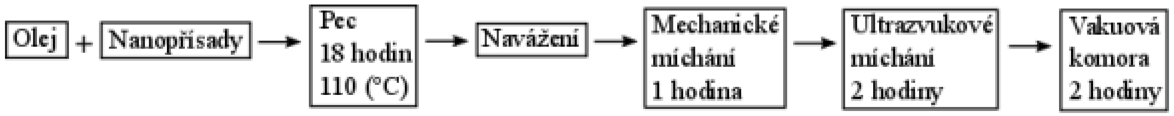
The pros and cons

- **Pros:**
- Improving of the selected properties
- Thermal conductivity, Resistivity, BDV

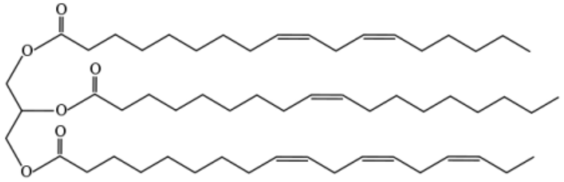
- **Cons:**
- Sedimentation a agglomeration
- Compatibility

- Homogeneously dispersed nanoparticles are a prerequisite for stable nanofluid
- Nanoparticles will remain dispersed if the Van der Waals forces are compensated by repulsive forces (respectively forces acting against attractive forces) such as electrostatic steric or electro-steric forces.

Obr. 5.3 Míchadlo s dvojitou šroubovicí



Obr. 5.7 Schematický postup výroby fluidního systému s nanopřísadami



Obr. 4.5 Strukturální vzorec řepkového oleje

Nanofluid with Envitrafol

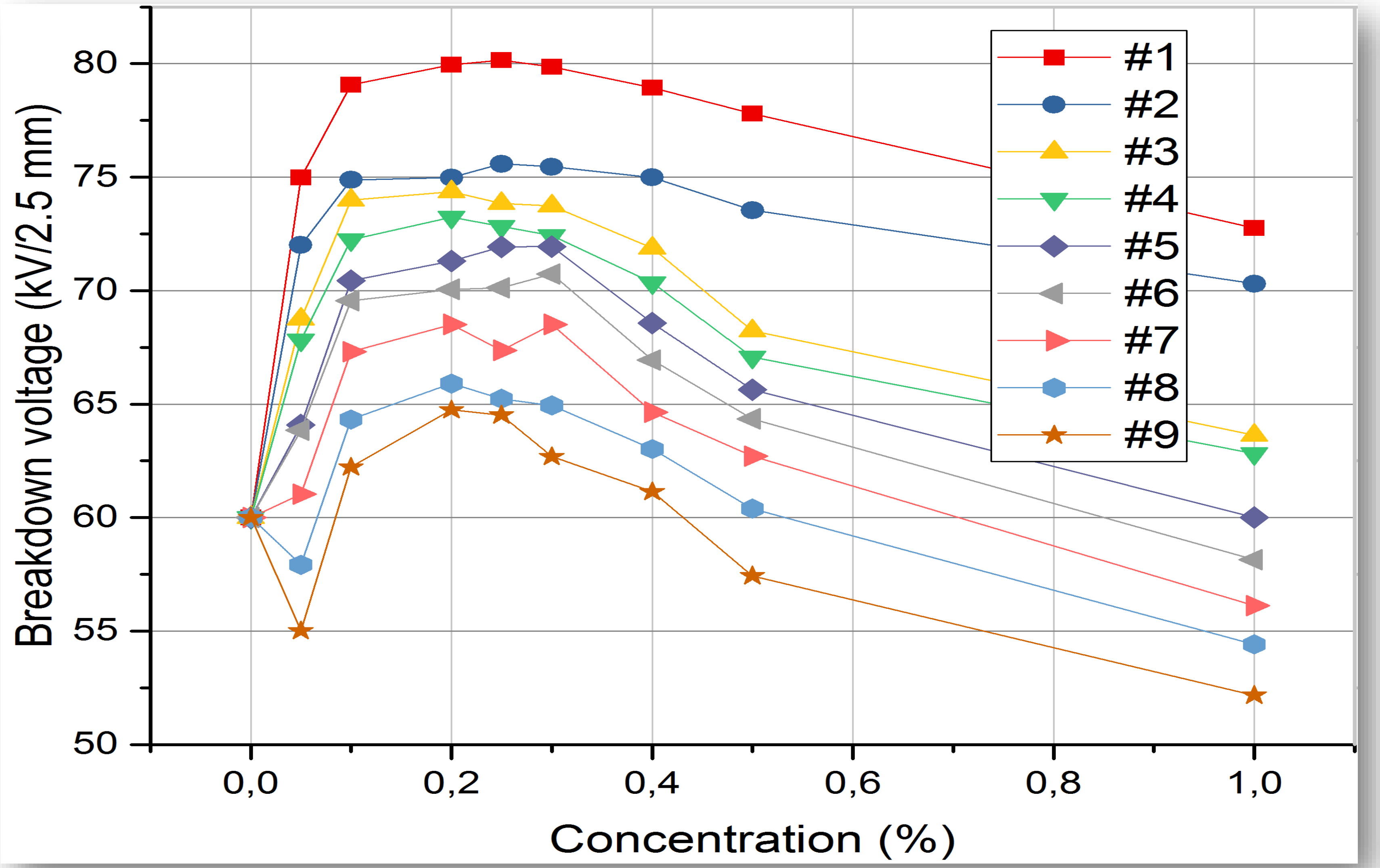
Generally

- These forces are important for the stability because they form a barrier that the particle must overcome in order to interact and create agglomerates with other particles. If the energy of this barrier is greater than the kinetic energy of the particle, the solution remains stable and homogeneously dispersed.
- In practice, to improve the stability of the nanoparticle, surfactants are used, i.e. surface treatments that reduce the surface tension in the liquid acting at the interface between the particles and the liquid. This interface determines the forces (mainly steric) acting on the formation of bonds between the particles. When using a surface treatment, it is necessary to select the proper type based on the application (not all surfactants interact suitability with the liquid) and then the proper amount, because too large amount of surfactant leads to "bubble creation" around the particle that easily captures the surrounding parts, which again leads to the formation of agglomerates.

Envitrafol Based Nanofluids #1

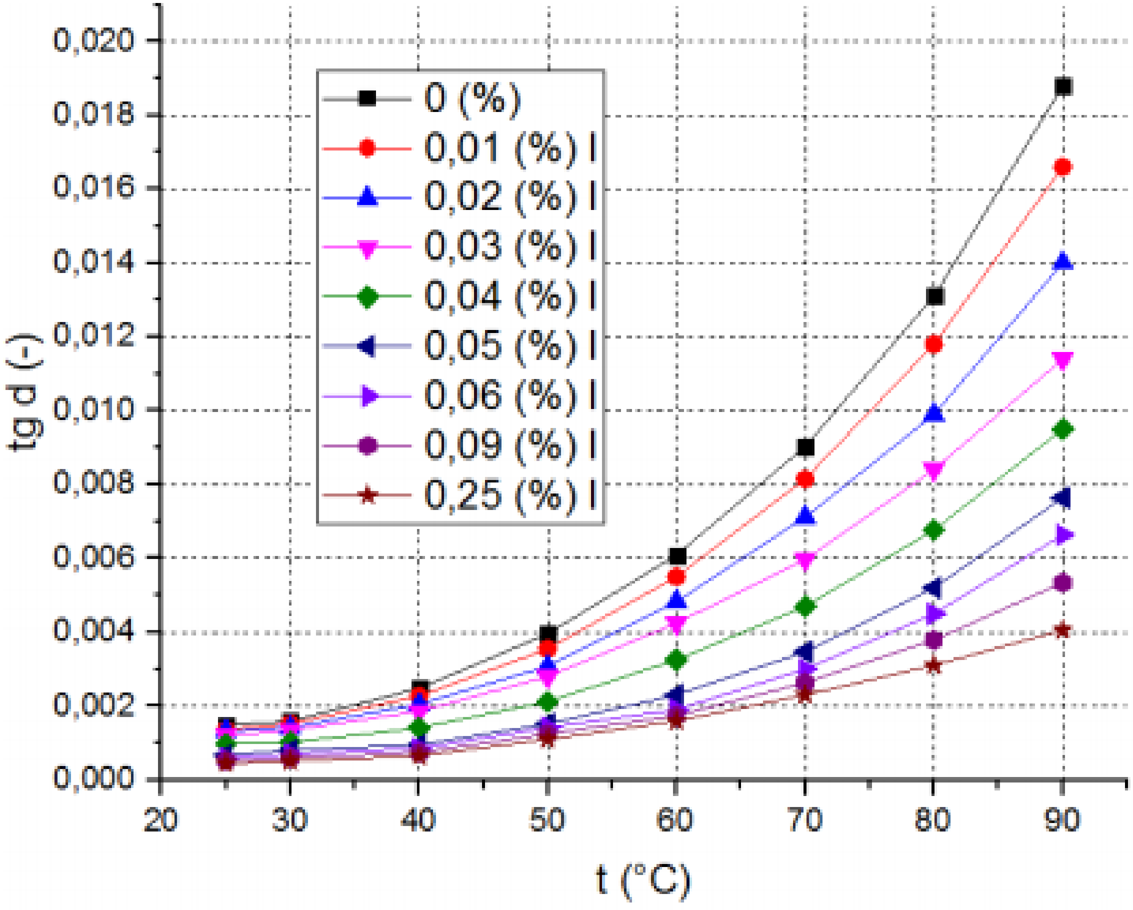
#	Nanofiller	Surface Treatment	Primary Particle Size (nm)	Max. Breakdown Voltage BDV (kV/2,5 mm)	Weight Content at max. BDV (%)
1	TiO_2	SiO_2	20	80,1	0,25
2	TiO_2	-	20	75,6	0,25
3	Al_2O_3 - γ	-	10	74,3	0,2
4	Al_2O_3 - γ	-	20 – 30	73,2	0,2
5	ZnO	-	20	72	0,3
6	ZnO	(3-Aminopropyl) triethoxysilan	30	70,8	0,3
7	ZnO	-	30	68,5	0,2
8	SiO_2	(3-Aminopropyl) triethoxysilan	20	65,9	0,2
9	SiO_2	-	30	64,5	0,2

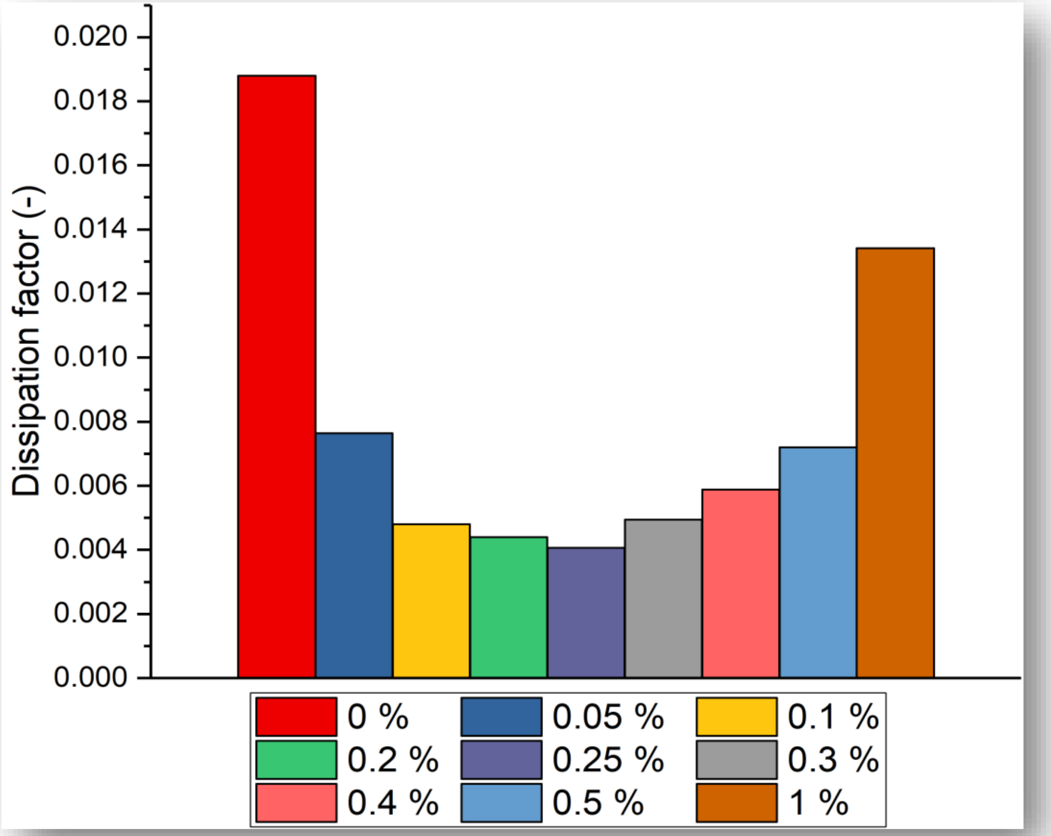
BDV #1



#	Nanofiller
1	TiO_2
2	TiO_2
3	Al_2O_3 - γ
4	Al_2O_3 - γ
5	ZnO
6	ZnO
7	ZnO
8	SiO_2
9	SiO_2

Dissipation Factor of Nanofluid ST TiO_2 #1





90°C

Volume resistivity of Nanofluid ST TiO_2 #1

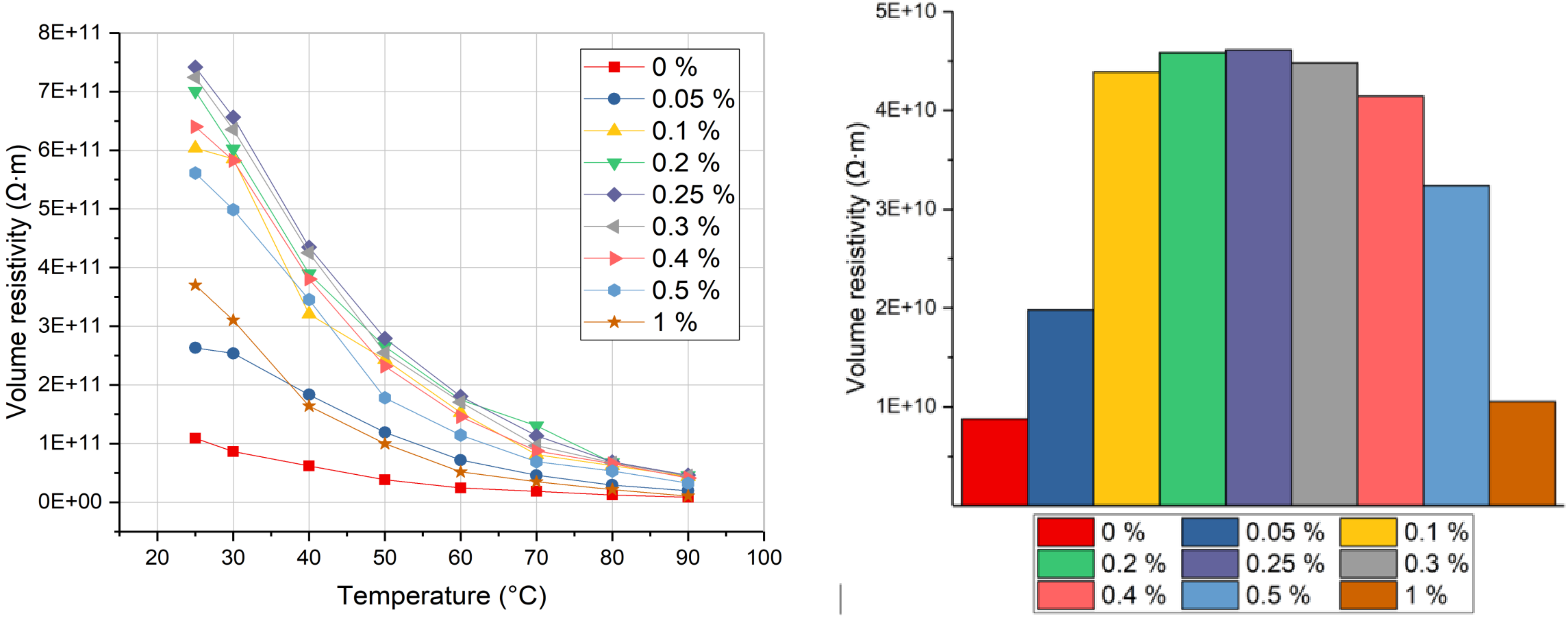
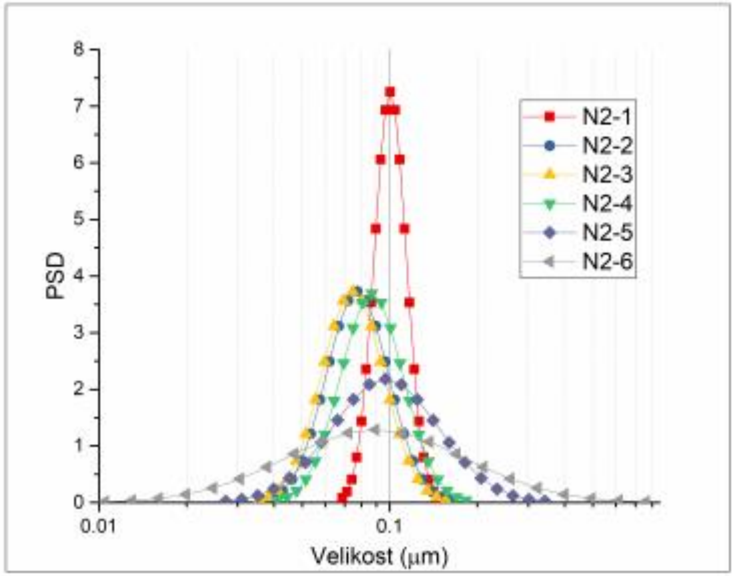


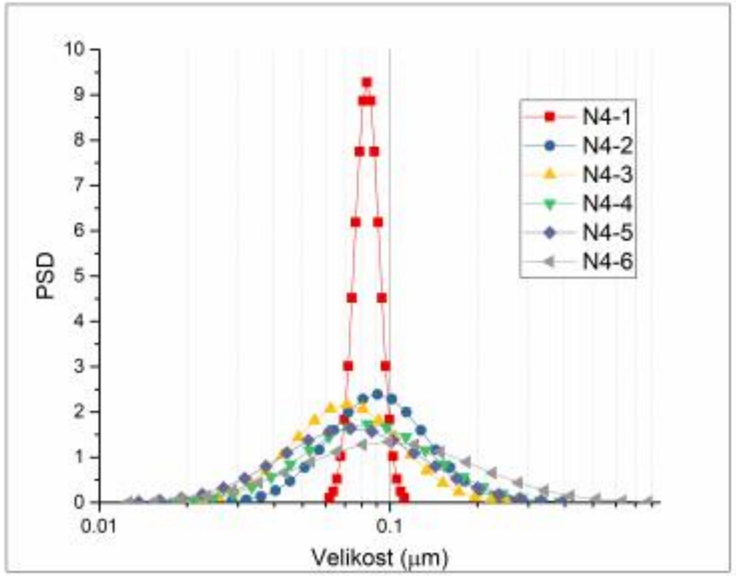
Figure 10. Dependence of volume resistivity of nanofluid with ST TiO_2 on nanoparticle concentratio
90 °C

Rapeseed MgO nanofluid #2

Agglomeration in 20 Days, using DT-1200 Spectrometre



Obr. 39: Disperze vzorku N2 v čase



Obr. 40: Disperze vzorku N4 v čase

Tab. 17: Přehled označení experimentálních vzorků

Koncentrace \ Surfaktant	S1	S2	S3	žádný
1.0 g/l	N1	N2	N3	N4
1.5 g/l	N5	N6	N7	N8
2.0 g/l	N9	N10	N11	N12

Source: Totzauer: DDP, Aspekty používání biodegradabilních elektroizolačních kapalin, ZČU, 2019

Conclusions

Nanofluids

- Further improving of the dielectric properties is achievable
- Nanoscale dielectric phenomena explanation
- Compensation of the higher space charge in natural esters
- The open question for use in electrical machinery is the issue of sedimentation and „filtering“ on the particles

TiO_2 ε_r =100 (Rutile)

BDV of nanometric layer TiO_2 = 270 kV/mm

E_L=30.E

$BDV_{ENVITRAFOL}$ = 24 kV/mm

FAKULTA ELEKTROTECHNICKÁ
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V PLZNI

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