InComEss

Innovative polymer-based composite systems
for high-efficient energy scavenging and storage

This project receives funding in the European Commission’s Horizon 2020 Research Programme under Grant Agreement Number 862597

Training Material on polymer-carbon nanotube composites for thermoelectric applications


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ipf

IPF in the frame of the InComEss project

The InComEss project proposes a new green and cost-effective strategy for high efficient energy harvesting

by combining new smart advanced polymer-based composite materials and structures into a single/multi-source concept to harvest electrical energy from mechanical energy and/or waste heat ambient sources, which consists of three novel Energy Harvesting Systems (EHSs) configurations: Piezoelectric, Thermoelectric and hybrid Thermo/PiezoElectric EHSs.

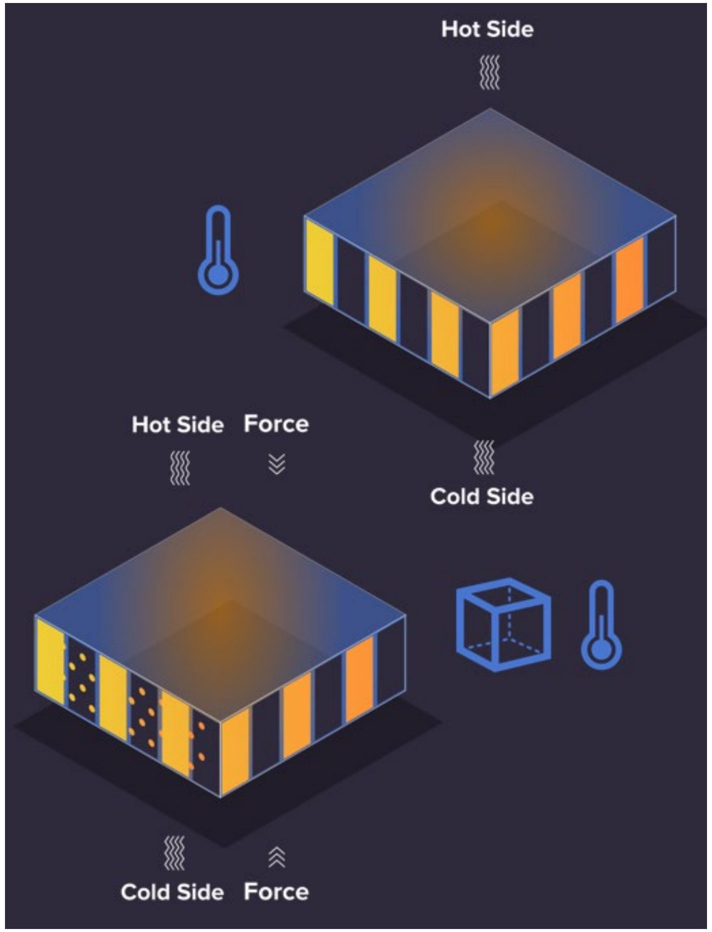
IPF will develop new materials

- **Innovative high-performance thermoplastic-based p-and n-type thermoelectric composites by using the Seebeck effect**

to be applied in

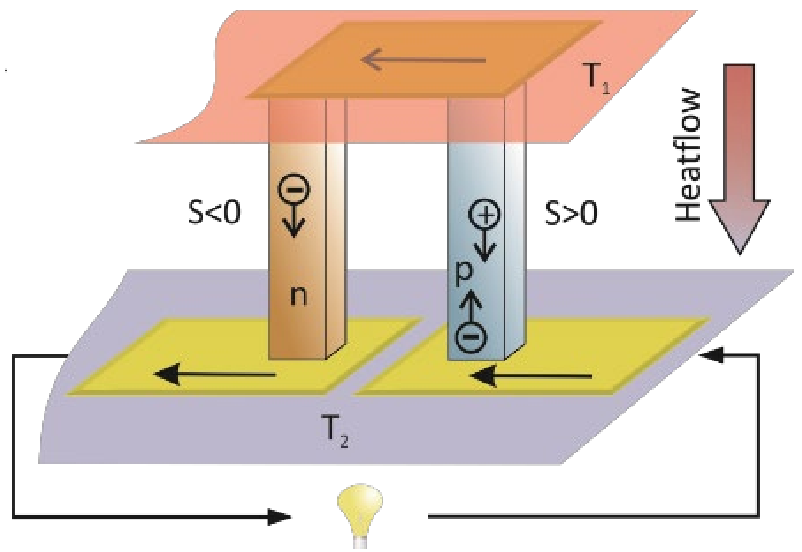
→ Single thermoelectric generators (TEGs)

→ Hybrid thermo-/piezoelectric generators (TPEGs)



Seebeck/thermoelectric effect

Thermoelectric (TE) effect is the direct conversion of temperature differences to electric thermovoltage and vice versa



$$S = \frac{U}{dT} \qquad PF = S^2\sigma \qquad ZT = \frac{S^2\sigma}{\kappa}T$$

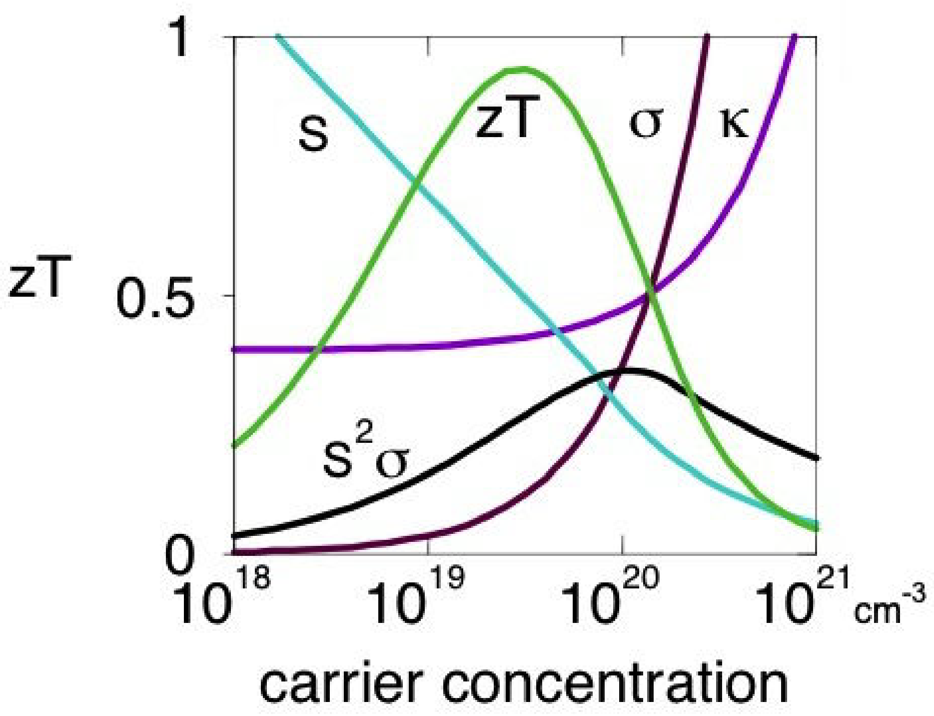
Seebeck coefficient S is a material constant

S = Seebeck coefficient [µV/K]
U = thermovoltage [V]
dT = temperature difference [K]
PF = power factor [µW/(m·K²)]
σ = volume conductivity [S/m]
ZT = figure of merit [-]
κ = thermal conductivity [W/m·K]
T = temperature [K]

Discovered by Thomas Johann Seebeck in 1821

Seebeck/thermoelectric effect

Correlations between TE parameters

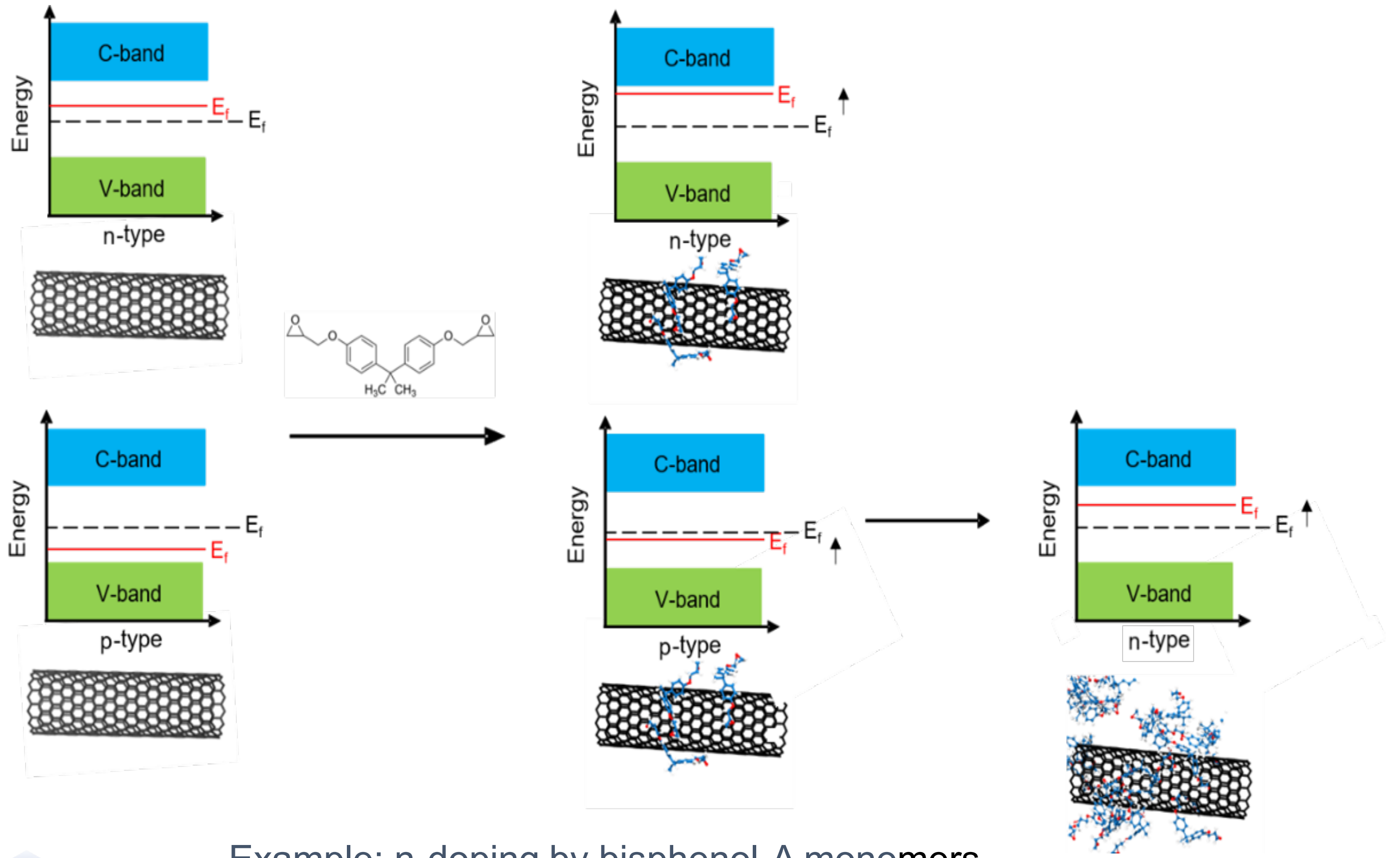


- Thermoelectric parameters are dependent on carrier concentration
- Opposite trend of Seebeck coefficient and volume conductivity
- Maximum for PF and ZT exists at different carrier concentrations

S = Seebeck coefficient
PF = Power factor $S^2\sigma$
σ = Volume conductivity
ZT = Figure of merit
κ = Thermal conductivity

Seebeck/thermoelectric effect

- **Shift of Fermi energy E_f level of CNTs through doping with molecules**
- → change of conduction type



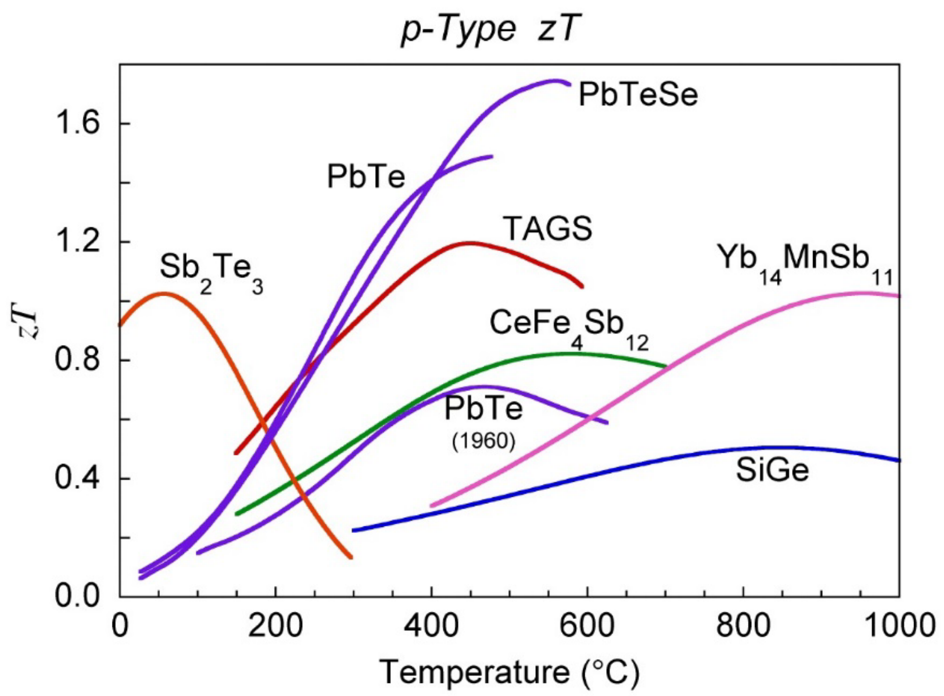
- **p-doping** shifts the Fermi energy towards the valence (V)-band due to the increased number of positive charge carriers (holes)
- n-doping shifts E_f nearer to the conduction (C)-band due to the increased number of negative charge carriers (de-localized electrons)

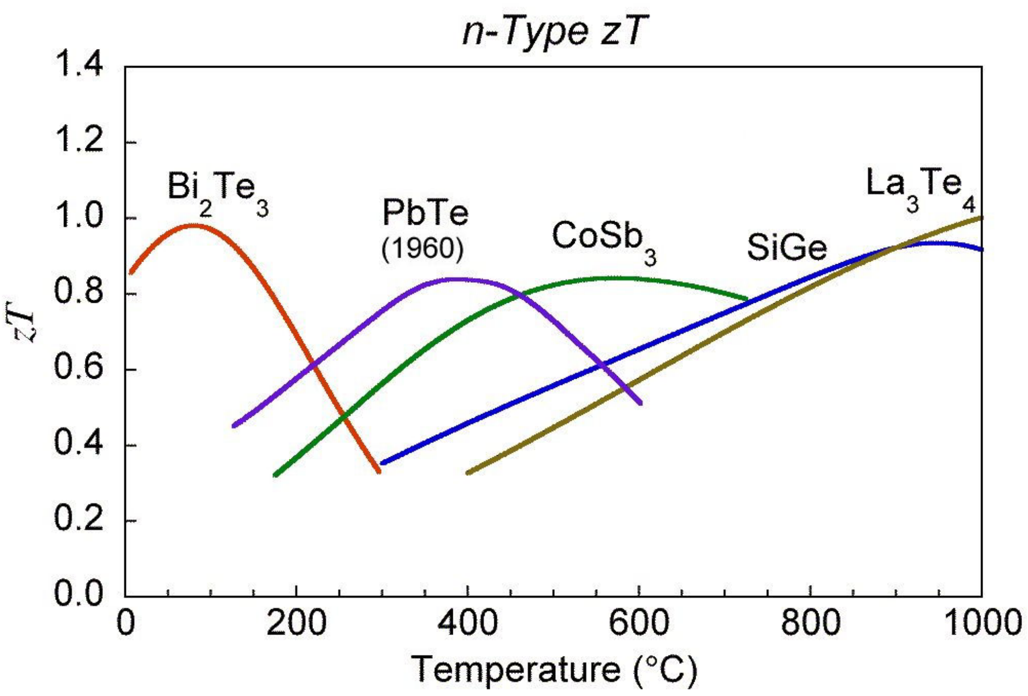
Example: n-doping by bisphenol-A monomers

Katharina Kröning, Beate Krause, Petra Pötschke, Bodo Fiedler, Nanocomposites with p- and n-Type Conductivity Controlled by Type and Content of Nanotubes in Thermosets for Thermoelectric Applications, **Nanomaterials 2020**, 10(6), 1144.

Seebeck/thermoelectric effect

Typical materials for TE generators



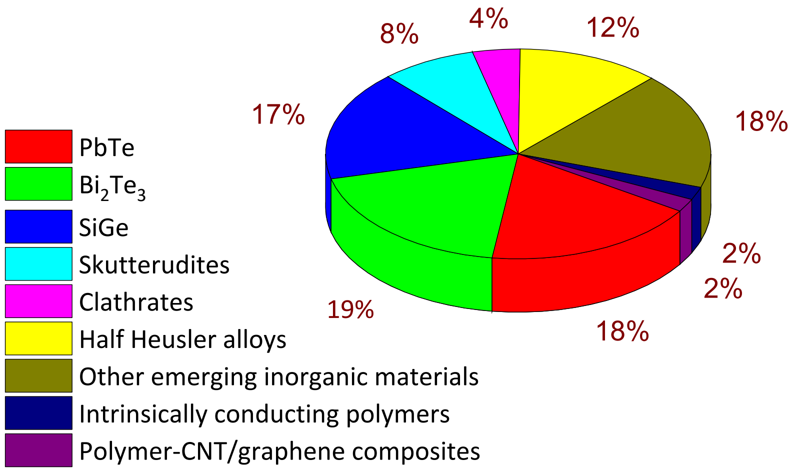


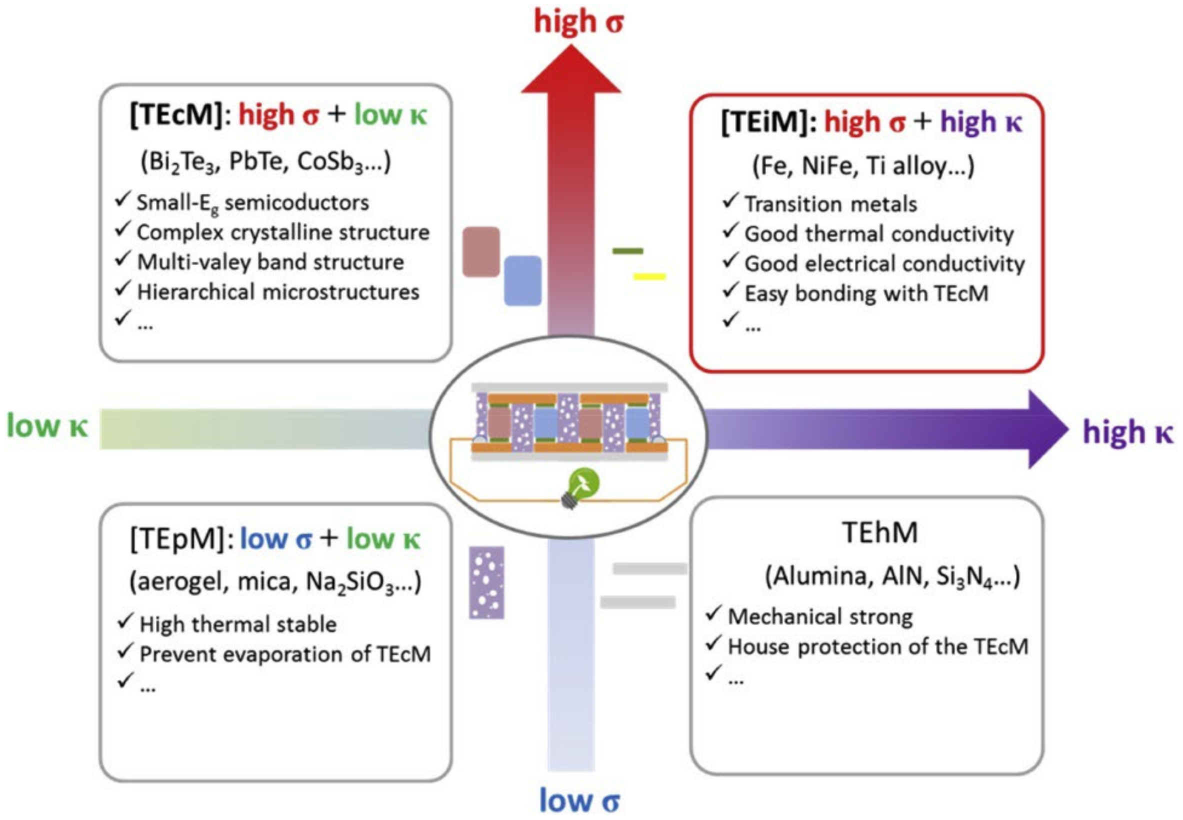
Typical materials: semiconductors, oxides, Half-Heusler-compounds, clathrates, silizides, antimonides, tellurides

Source: https://thermoelectrics.matsci.northwestern.edu/thermoelectrics/index.html

Seebeck/thermoelectric effect

Typical materials for TE generators



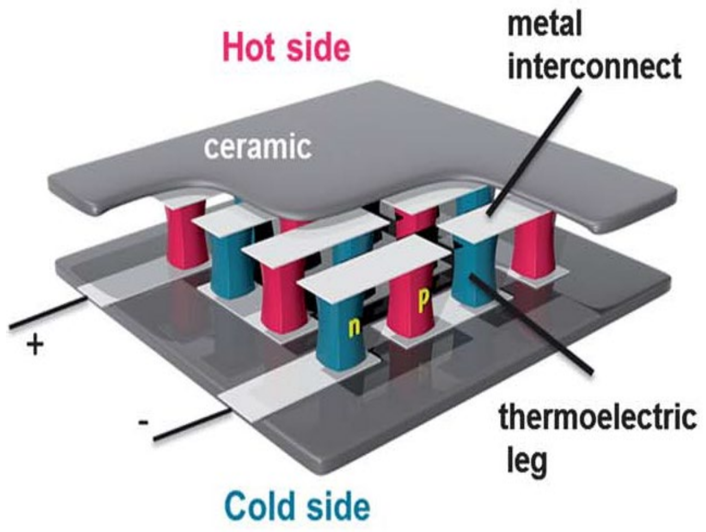


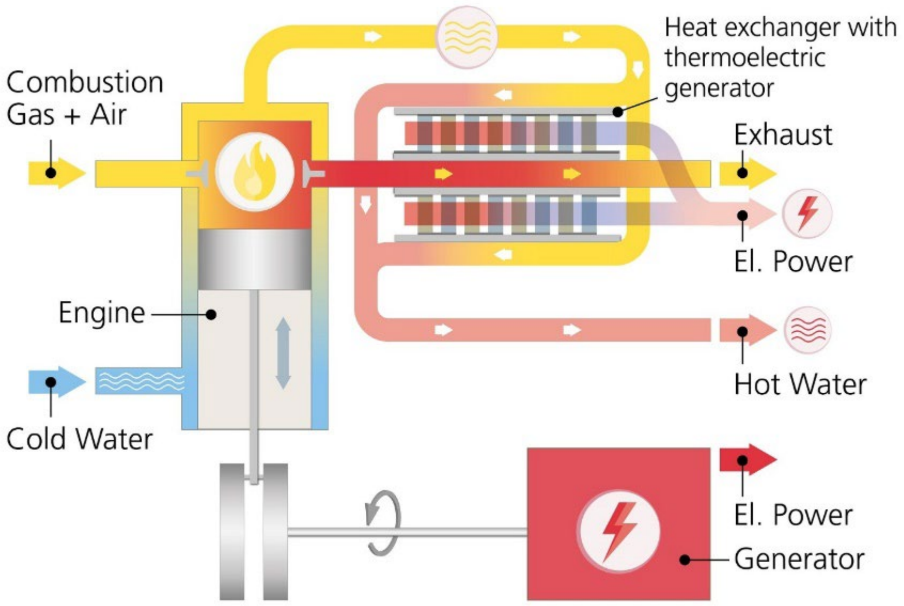
W. Liu et al. Journal of Materiomics 2019, 5 (3), 321-336; *C. Gayner, K.K. Kar, Progress in Materials Science 83 (2016) 330-382;* J. Snyder, E. S. Toberer, Complex thermoelectric materials, Nat. Mat., 2008, 7, 105-114

Seebeck/thermoelectric effect

Typical design and application for thermoelectric generators (TEGs)

TEG design using metal-based materials





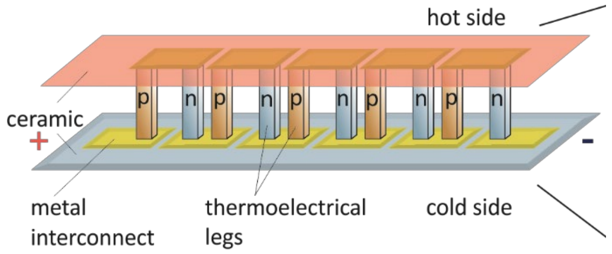
- Portable generator
- Use of waste heat

O. Bubnova, X. Crispin, Energy Environ. Sci., 2012, 5, 9345; https://www.ipm.fraunhofer.de/en/bu/energy-converters-thermal/expertise/thermoelectric-modules-and-systems/waste-heat-conversion.html

Seebeck/thermoelectric effect

Advantages of thermoelectric energy harvesting

- No movable parts, silent, no vibrations
- Unlike solar cells, thermoelectric generators can be used throughout the day
- Can harvest waste energy from environmental heat, waste heat in industry and household, body heat, etc.
- Environmentally friendly, easy maintenance



Disadvantages of typical semiconductors (metal based)

- Expensive materials
- Partially toxic, contain rare earth elements, geopolitical supply risk
- Difficulties in processing, highly energy consuming

Classification of polymer based TE materials

Intrinsically electrical conductive (C) polymers (ICP)
PEDOT:PSS, polyaniline, P3HT, not meltable, solution processable, printable…

- without additional TE or C fillers
- with additional TE or C fillers (e.g.Bi_2Te_3 or CNT)

Composites of non-conductive matrix with conductive filler (CPC)
thermoplastic or duroplastic polymers, rubbers; solution or melt processable with e.g. CB, CNT, graphene, metal powder, …

- without additional TE fillers
- with additional TE fillers (e.g.Bi_2Te_3, CuO, TiO_2, …..)

Melt processable thermoplastic matrices:
scalable to mass production, easy to be shaped

Petra Pötschke, Beate Krause, Jinji Luo, Melt-mixed thermoplastic polymer/carbon nanotube composites for thermoelectric applications, TechConnect Briefs, Volume: 1, Advanced Materials: TechConnect Briefs 2018, Pages: 196 – 199.

Seebeck/thermoelectric effect with polymers - State of the art

- Intrinsically conductive polymers, like PEDOT:PSS and PEDOT:Tos are widely studied

- **Melt mixed thermoplastic conductive polymer composites (CPCs)**
- Advantages of thermoplastic polymer composites:
  - High flexibility and adaptability (different shapes, incl. films, fibers, textiles...)
    → new designs for TEGs are possible
  - Favorable intrinsically low thermal conductivity (0.1-0.3 W/m·K)
  - Available, cheap and easy to process with existing processing methods
  - Lightweight, comparably environmental friendly
  - Stable materials (long term durable) and recyclable, no corrosion
- Disadvantages of thermoplasticpolymer composites:
  - Lower electrical conductivity and Seebeck coefficient than traditional materials
  - Usage only in temperature range -20°C up to 240°C

State of the art – thermoplastic CPCs

- Polymer based TE materials are under development
- Polymers have high flexibility and low thermal conductivity
- But show low electrical conductivity and Seebeck coefficient
- Intrinsically conductive polymers, like PEDOT:PSS and PEDOT:Tos are widely studied [1]
- Insulating polymers filled with conductive fillers mainly investigated as solution mixed composites, e.g. PVDF with SWCNTs [2,3]
- **Melt mixed conductive composites with conductive fillers mostly studied by our group and rarely by others**

[1] O. Bubnova, Z. U. Khan, A. Malti, and et al., Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylene oxythiophene), Nat. Mat., 2011, 10, 429-433

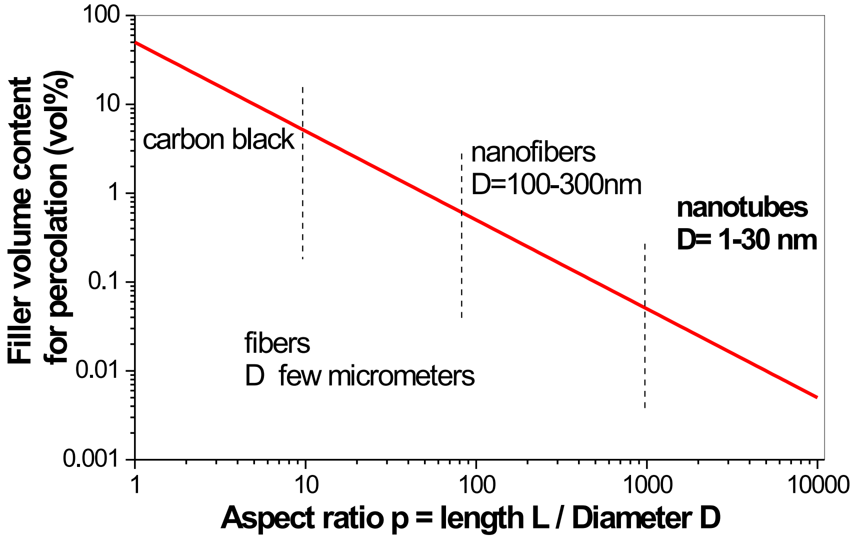
[2] C. A. Hewitt, A. B. Kaiser, S. Roth and et al., Varying the concentration of single walled carbon nanotubes in thin film polymer composites, and its effect on thermoelectric power, Appl. Phys. Lett., 2011, 98, 183110,
[3] A. B. Kaiser, Thermoelectric power and conductivity of heterogeneous conducting polymers, Phys. Rev. B, 1989, 40, 2806-2813

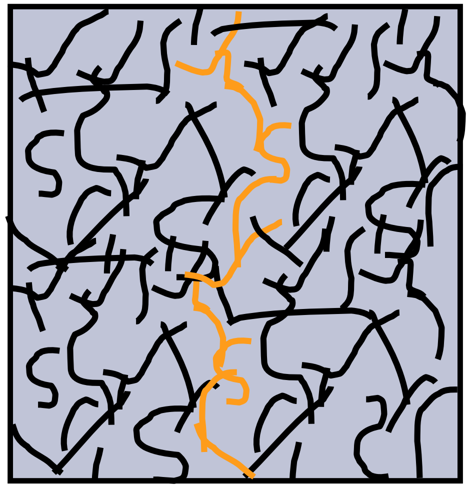
Composites of non-conductive matrix with conductive filler (CPCs)

Conductivity of the material is a condition to show the Seebeck effect

Conductivity is achieved if a percolated filler network is formed

- Fillers touch each other or hopping or tunneling of electrons between neighboring filler particles (ca. 10 nm)
- Percolation concentration as lower as higher filler aspect ratio - CNTs preferable

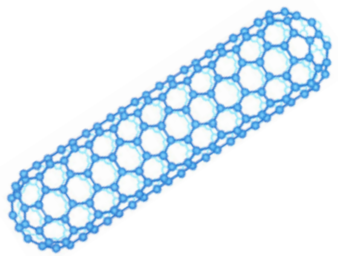


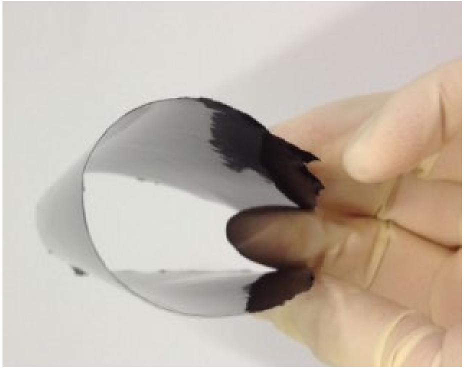


Focus of thermoelectric research at IPF Dresden

Basic investigations on factors influencing the thermoelectric properties of melt-mixed conductive thermoplastic nanocomposites filled with electrical conductive carbon-based nanofillers (content above filler percolation):

- **CNT type** and **concentration**
- **polymer matrix** type
- **Additives**
- **Variation of melt mixing conditions**





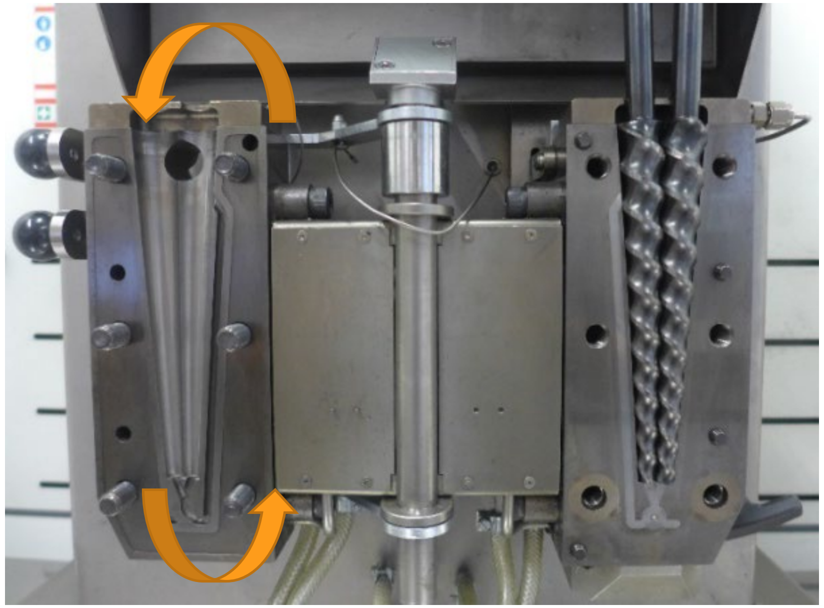
Recipe development

to achieve **p-** or **n-type** materials with high Seebeck coefficient and power factor

Nanocomposite Preparation

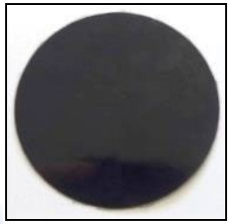
Small-scale melt compounding and shaping

- Xplore 15 microcompounder
  - → Temperatures up to 360°C
  - → Rotation speed up to 250 rpm
  - → Mixing time: 5-25 min
- Compression moulding typically at mixing temperature



circulation of the polymer melt in the chamber and bypass

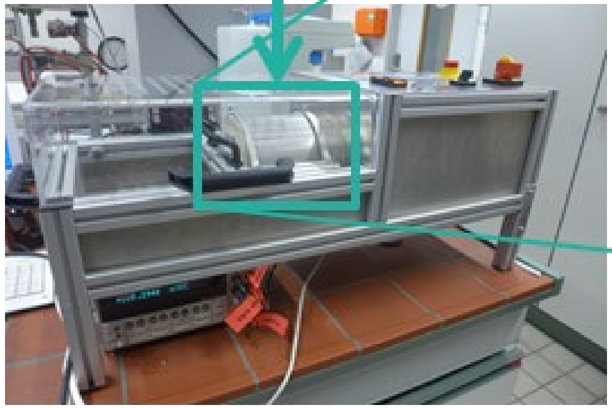
strands

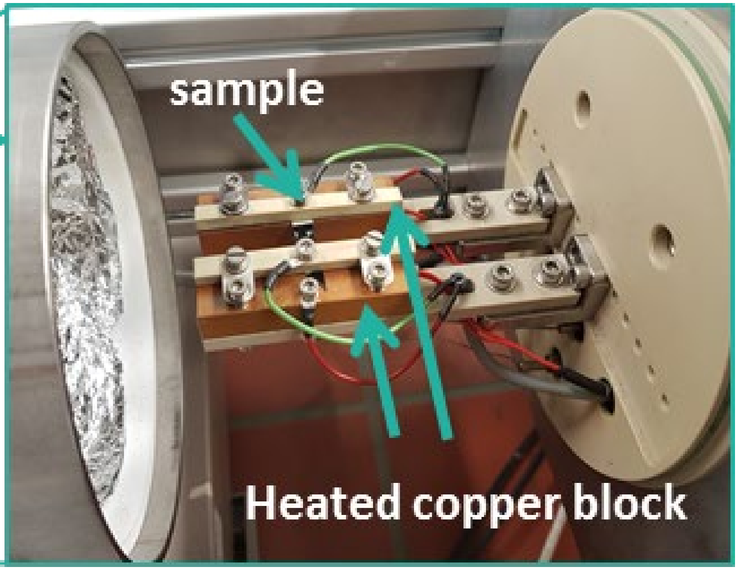


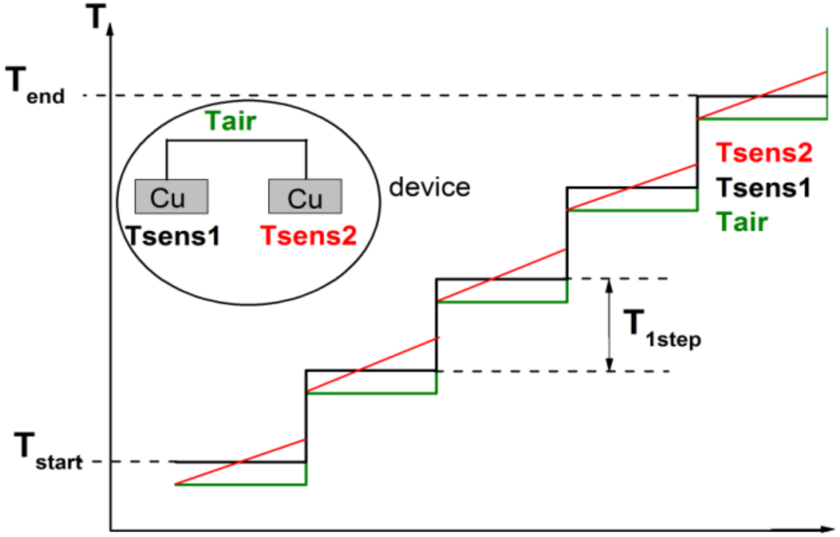
plates

Measuring set-up constructed & built at the IPF

Temperature controlled housing

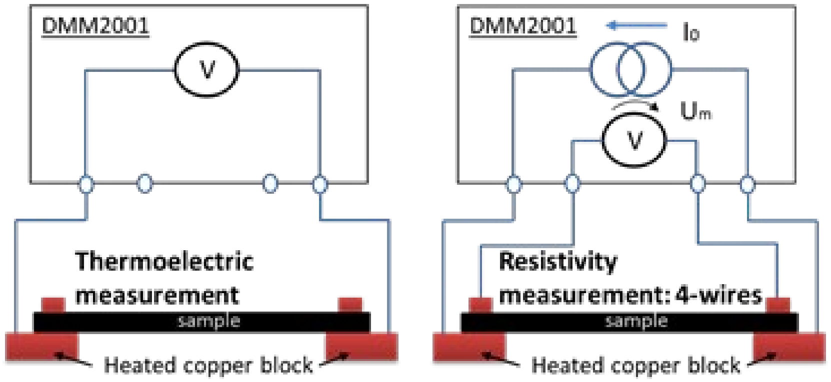






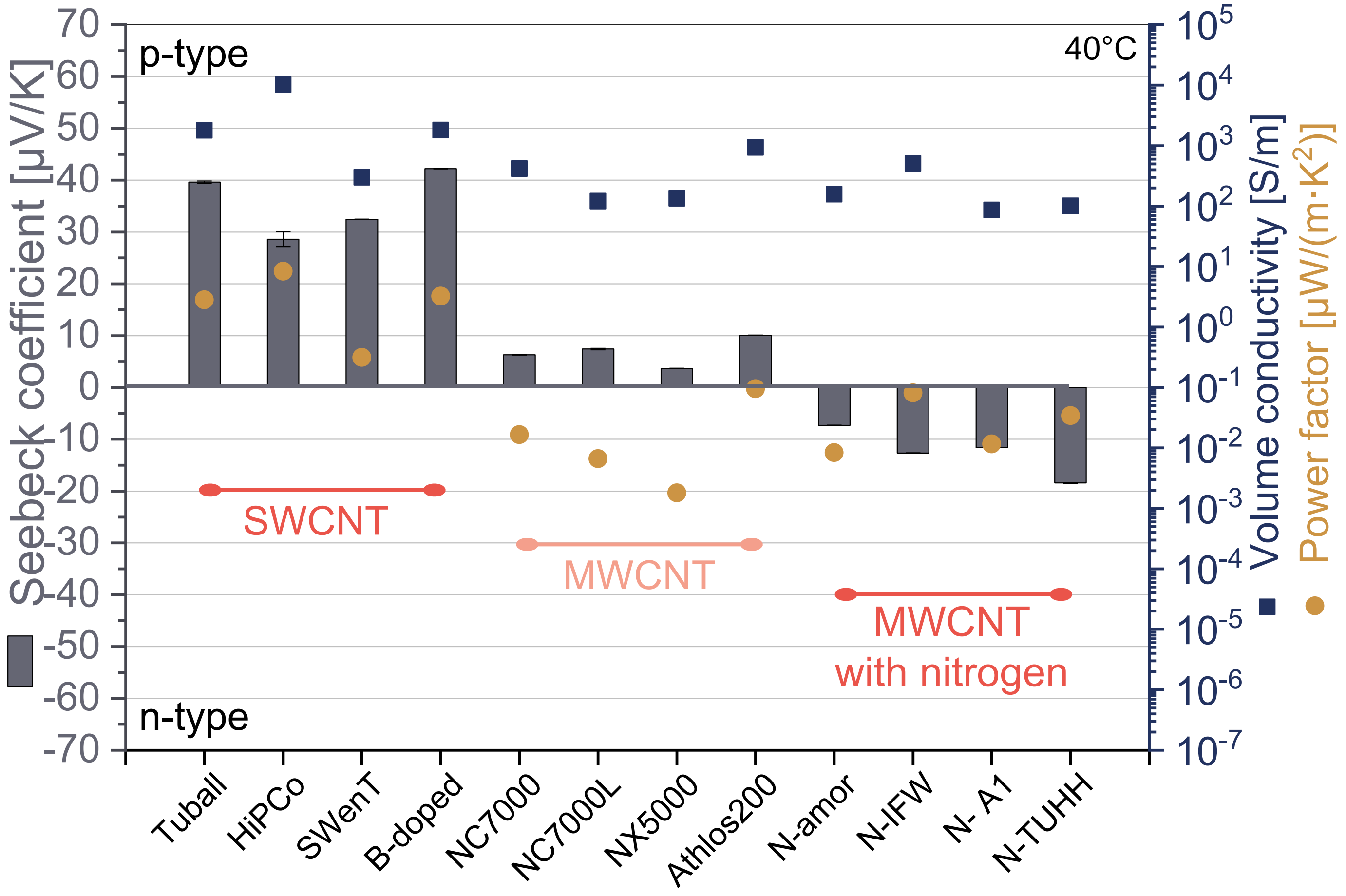
Measurements on solid samples and powders

Working temperature up to 110°C



W. Jenschke et al. **Technisches Messen 2020**, 87(7-8), 495-503; https://doi.org/10.1515/teme-2019-0152
M. Gnanaseelan et al., **Comp Sci Techn 2018**, *163*, 133-140, doi: 10.1016/j.compscitech.2018.04.026

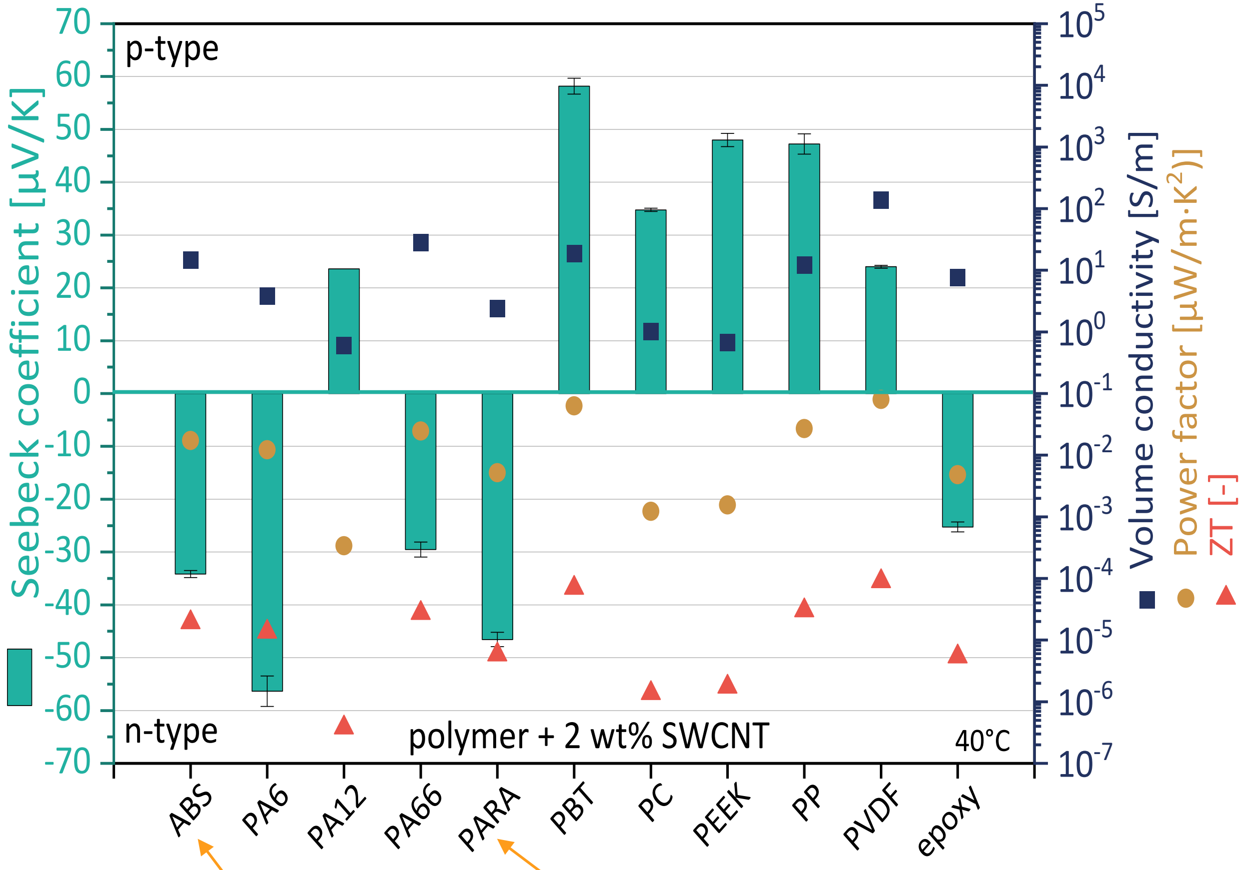
Influence of CNT-type (powder) on TE performance

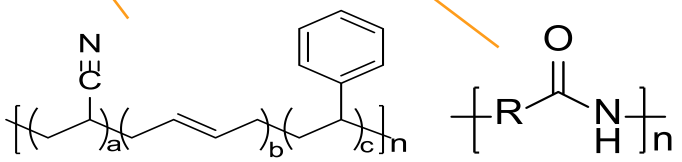


- Typically industrial CNTs have positive Seebeck coefficient
- Higher positive Seebeck coefficient values for SWCNTs than for MWCNTs
- Negative Seebeck coefficient values for nitrogen-doped MWCNTs

Kröning et al. Nanomaterials 10 (2020) 1144; Krause et al. J. Compos. Sci. 4 (2020) 14; Krause et al. Energies 13 (2020) 394; Krause et al. J. Compos. Sci. 3 (2019) 106; Luo et al. Polymer 108 (2017) 513;

Influence of polymer type on TE performance





- Mainly positive Seebeck coefficient values for polymer/SWCNT composites
- Negative Seebeck coefficient are found for PA and ABS composites → amide and nitrile groups, which can dope SWCNTs by insertion of electrons to make them n-type

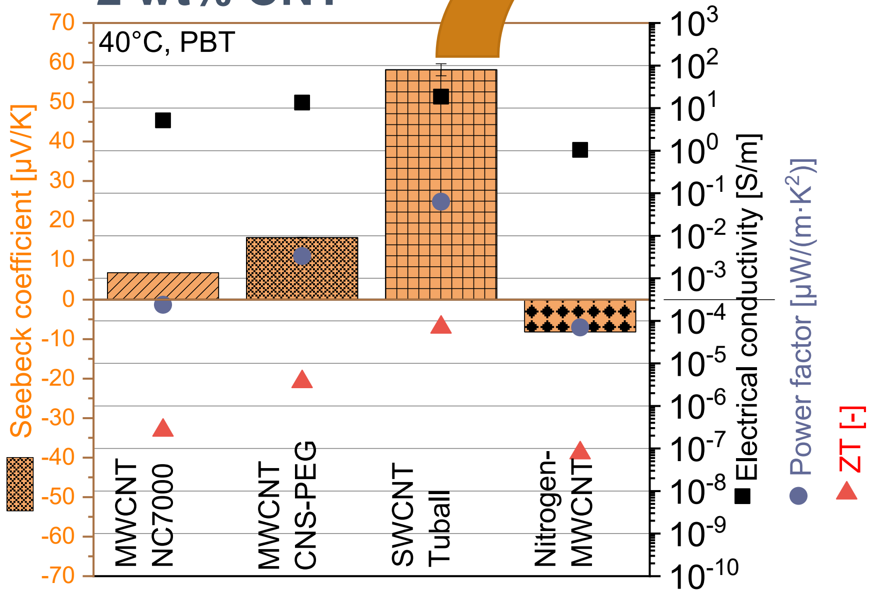
Kröning et al. Nanomaterials 10 (2020) 1144; Krause et al. J. Compos. Sci. 4 (2020) 14; Krause et al. Energies 13 (2020) 394; Krause et al. J. Compos. Sci. 3 (2019) 106; Luo et al. Polymer 108 (2017) 513;

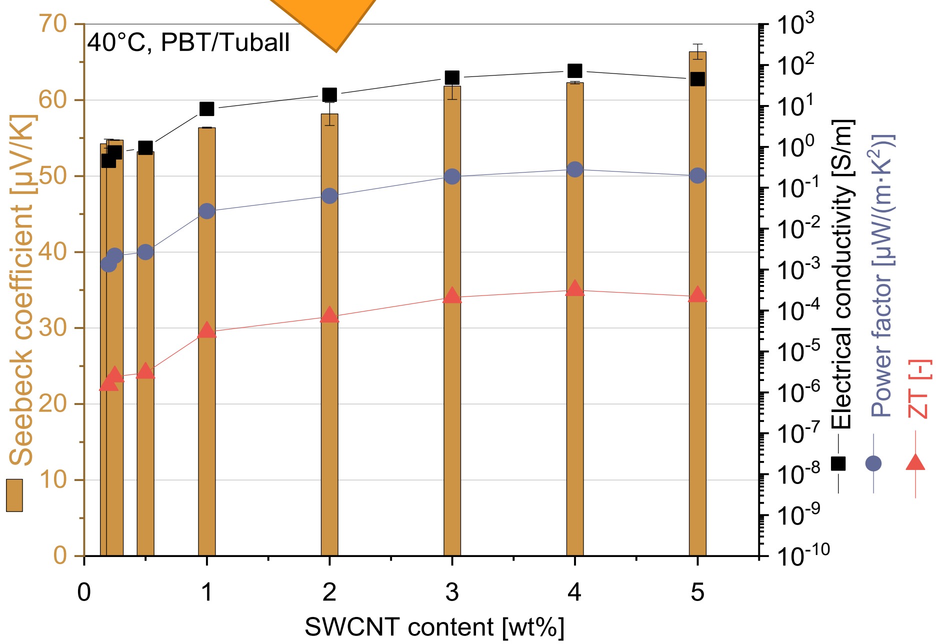
Combination effects of polymer and CNT type

PBT

power factor PF = $S^2 \cdot \sigma$
ZT = PF*T/κ
κ= 0.28 W/(m·K)

2 wt% CNT





- S values differ for CNT types, SWCNT > MWCNT,
- S-values of composites partially higher than of buckypapers

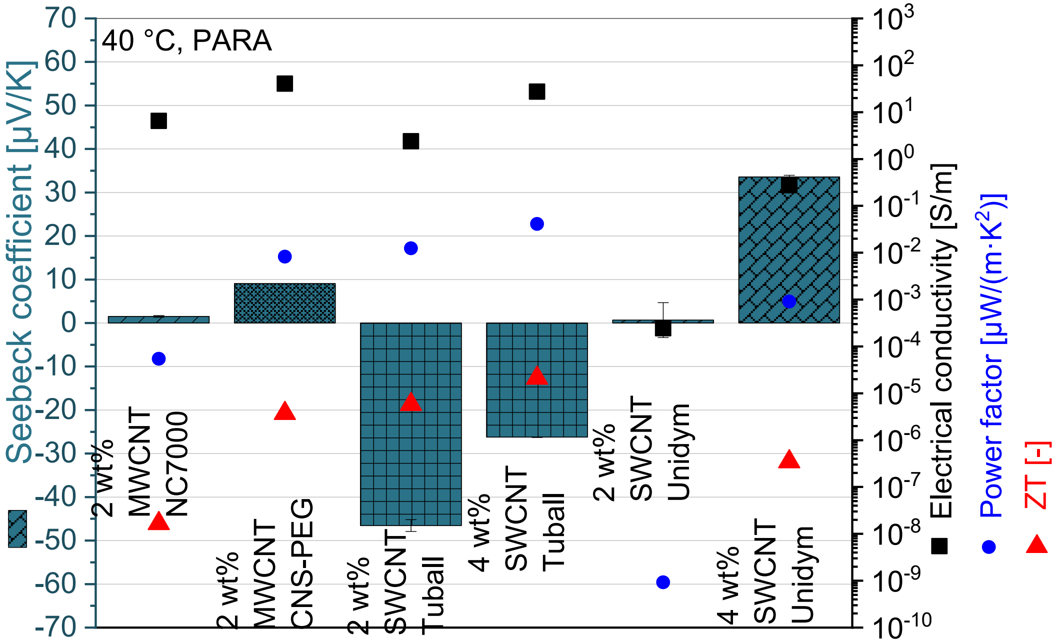
- S-value increases with SWCNT loading
- Electrical conductivity shows saturation at ca. 4 wt% loading as do PF and ZT

B. Krause, C. Barbier, J. Levente, M. Klaus, P. Pötschke, **Journal of Composites Science 2019**, 3(4), 106; https://doi.org/10.3390/jcs3040106

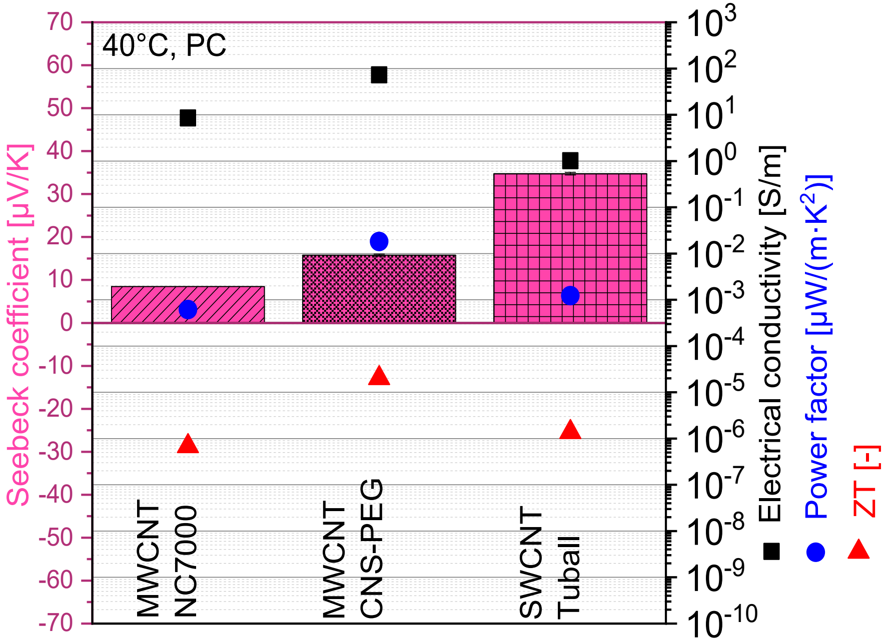
Combination effects of polymer and CNT type

PARA

2 wt% CNT



PC



power factor PF = $S^2 \cdot \sigma$
ZT = PF*T/κ
κ= 0.28 W/(m·K)

- S values differ for CNT types, SWCNT > MWCNT,
- S-values of composites partially higher than of buckypapers
- For SWCNT in PARA switching to negative S-values occurs
- PARA: S-values up to 35 µV/K and -45 µV/K; PC: up to 35 µV/K

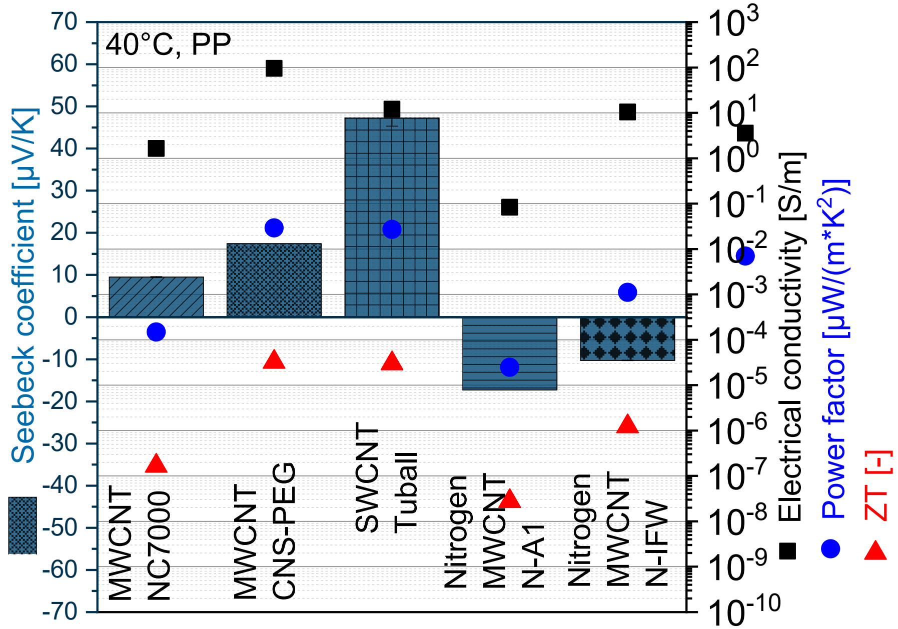
B. Krause, C. Barbier, J. Levente, M. Klaus, P. Pötschke, **Journal of Composites Science 2019**, 3(4), 106; https://doi.org/10.3390/jcs3040106

Combination effects of polymer and CNT type

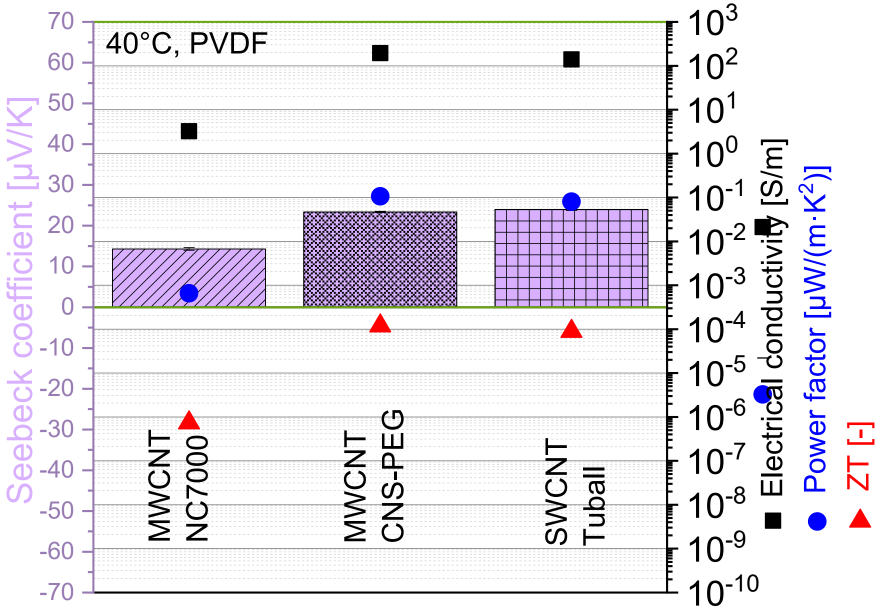
power factor PF = $S^{2} \cdot \sigma$
ZT = PF*T/κ
κ= 0.28 W/(m·K)

PP

2 wt% CNT



PVDF



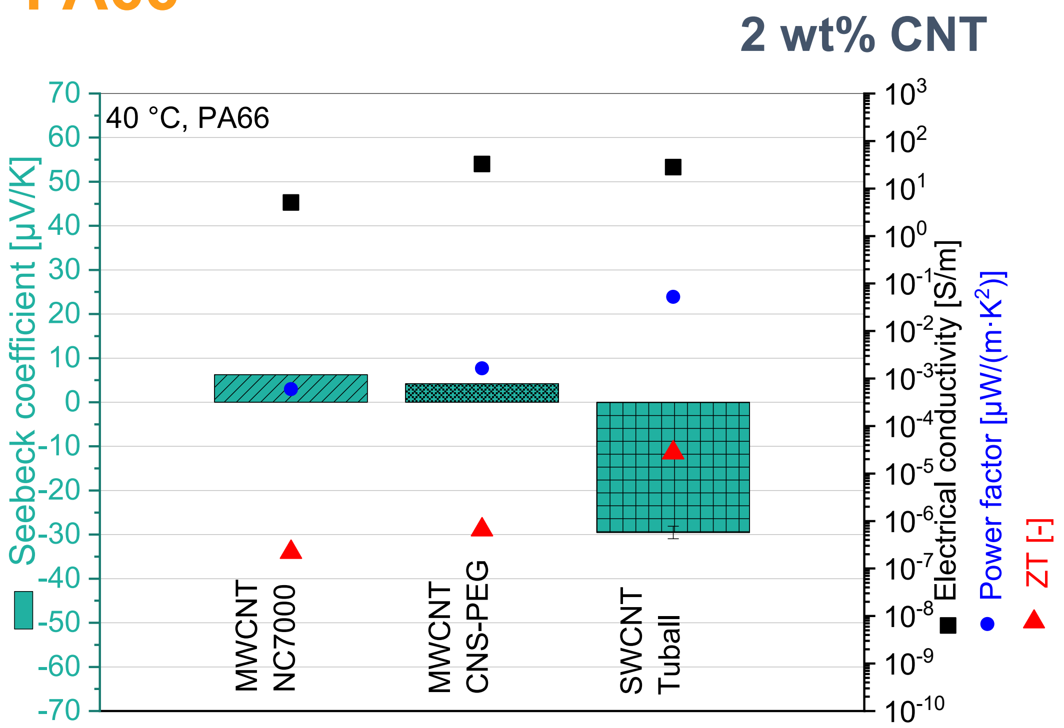
- S values differ for CNT types, SWCNT > MWCNT,
- S-values of composites partially higher than of buckypapers
- PP: negative S-values reached if nitrogen-doped MWCNT were used
- PP: S-values up to 50 µV/K and -15 µV/K; PVDF: up to 25 µV/K

B. Krause, C. Barbier, J. Levente, M. Klaus, P. Pötschke, **Journal of Composites Science 2019**, 3(4), 106; https://doi.org/10.3390/jcs3040106

Combination effects of polymer and CNT type

PA66

power factor PF = $S^2 \cdot \sigma$
ZT = PF*T/κ
κ= 0.28 W/(m·K)



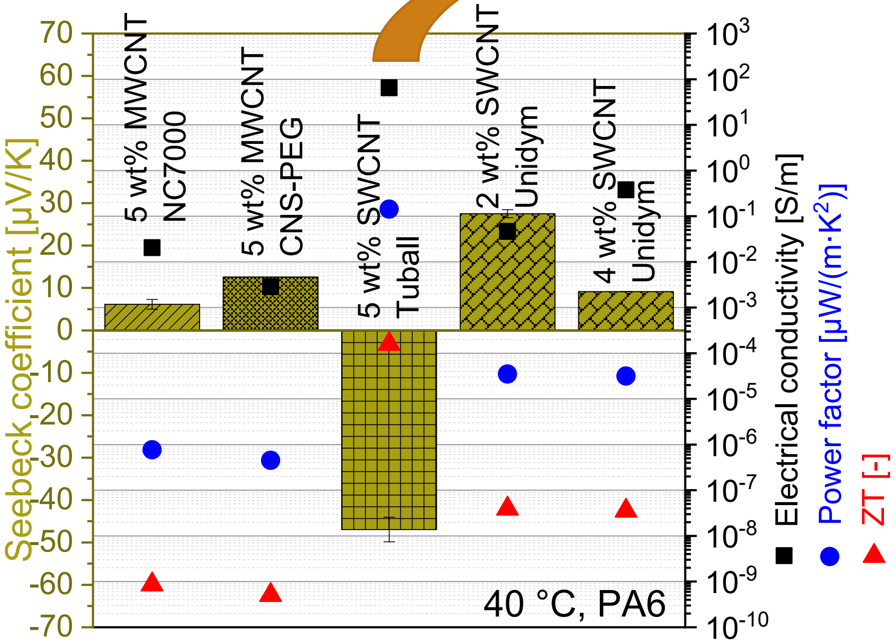
- For SWCNT Tuball in PA66 switching to negative S-values occurs
- However, SWCNT Unidym positive S-values (with decreasing tendency when content is increased)

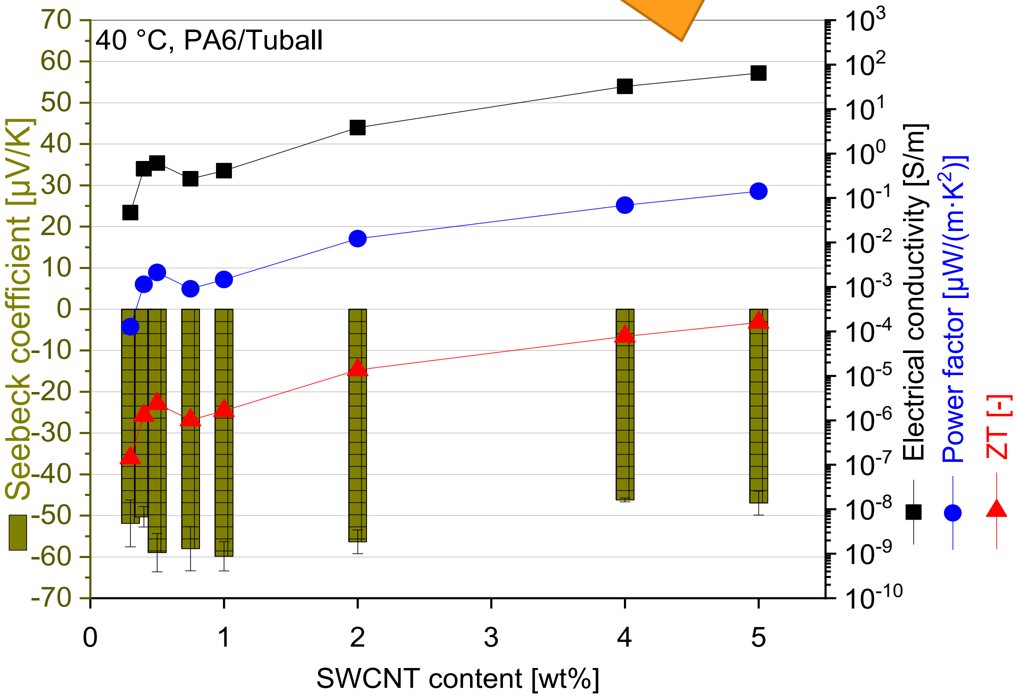
B. Krause, C. Barbier, J. Levente, M. Klaus, P. Pötschke, **Journal of Composites Science 2019**, 3(4), 106; https://doi.org/10.3390/jcs3040106

Combination effects of polymer and CNT type

PA6

power factor PF = $S^2 \cdot \sigma$
ZT = PF*T/κ
κ= 0.28 W/(m·K)





- For SWCNT Tuball negative S-values
- However, SWCNT Unidym positive S-values (with decreasing tendency when content is increased)

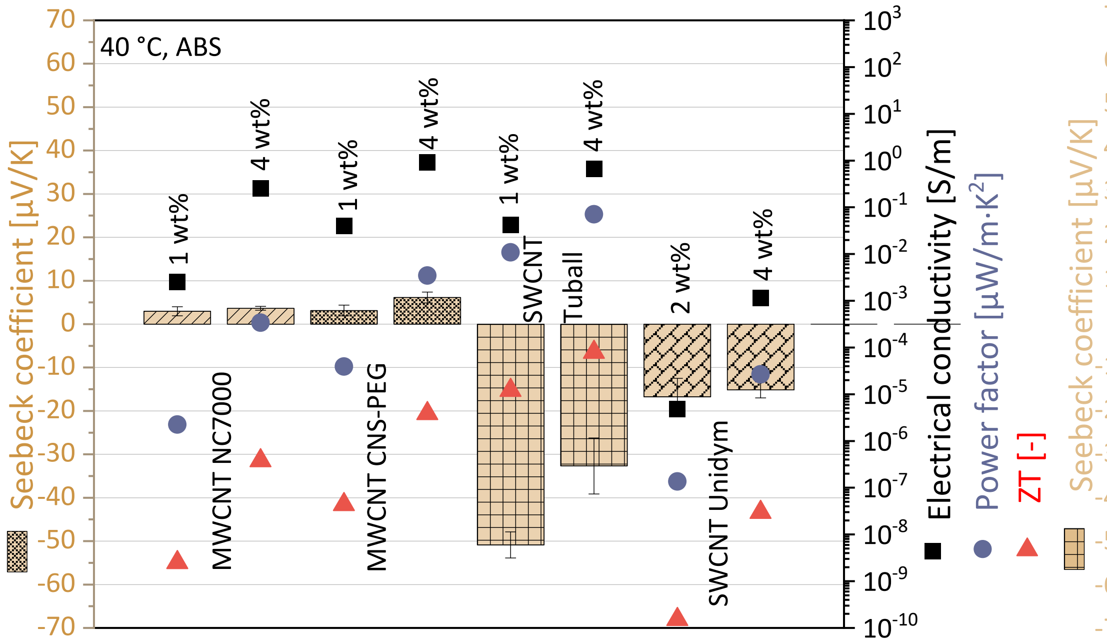
- Highest negative S-values at 0,5-1 wt%
- Electrical conductivity, PF and ZT increase with SWCNT content

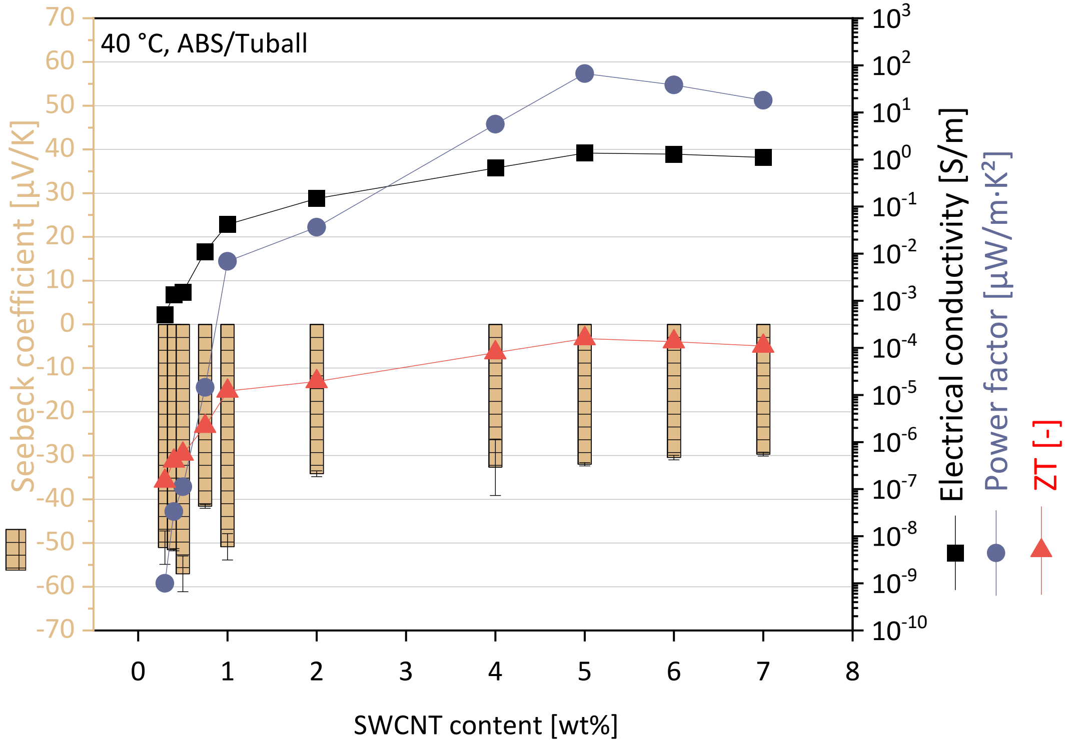
B. Krause, C. Barbier, J. Levente, M. Klaus, P. Pötschke, **Journal of Composites Science 2019**, 3(4), 106; https://doi.org/10.3390/jcs3040106

Combination effects of polymer and CNT type

ABS

power factor PF = $S^{2} \cdot \sigma$
ZT = PF*T/κ
κ= 0.28 W/(m·K)





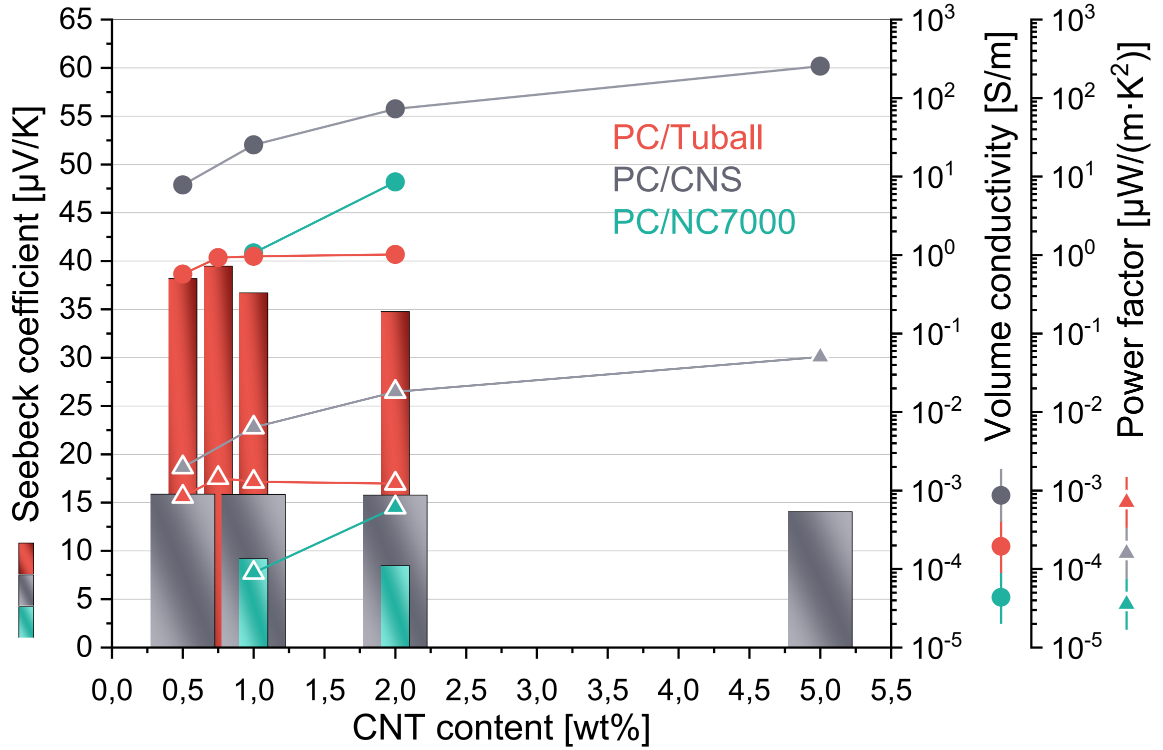
- For SWCNT negative S-values
- Positive S-values for MWCNT

- Highest negative S-values at 0.5 wt%
- Electrical conductivity, PF and ZT show saturation at 5 wt% loading

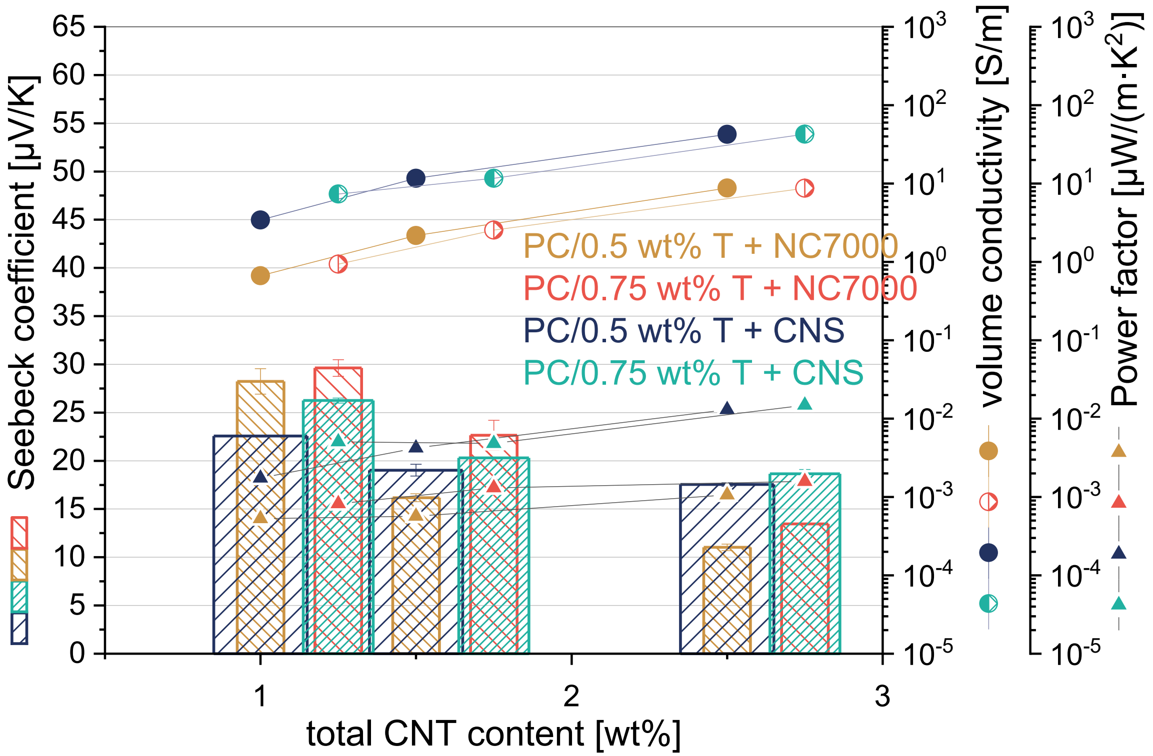
B. Krause, C. Barbier, J. Levente, M. Klaus, P. Pötschke, **Journal of Composites Science 2019**, 3(4), 106; https://doi.org/10.3390/jcs3040106

Combination effects of polymer and different CNT types: PC

One kind of CNT



Hybrid CNT fillers



- Highest S-value for PC/SWCNT Tuball
- Highest conductivity for PC/CNS (branched MWCNT)

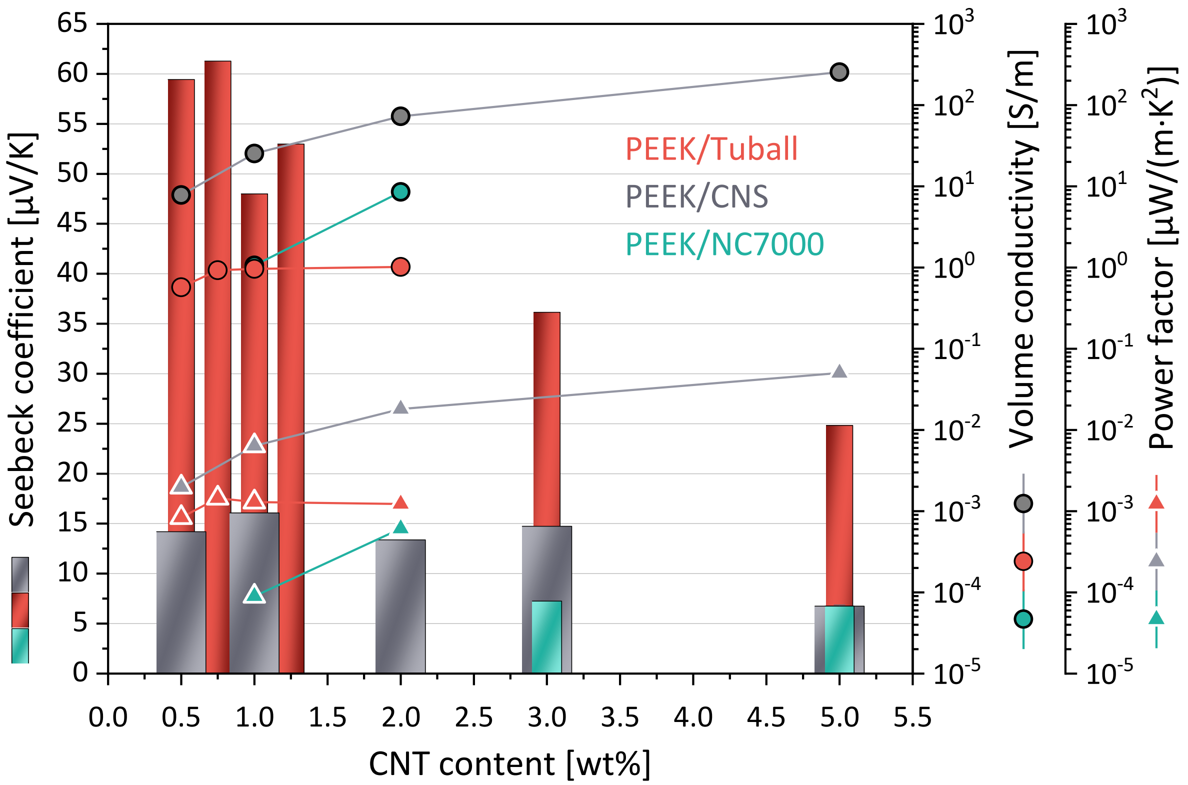
- All thermoelectric parameters are lower compared to single filler composites

I. Konidakis, B. Krause, G.-H. Park, N. Pulumati, H. Reith, P. Pötschke, E. Stratakis, **ACS Applied Energy Materials** 2022, 5, 9770−9781.

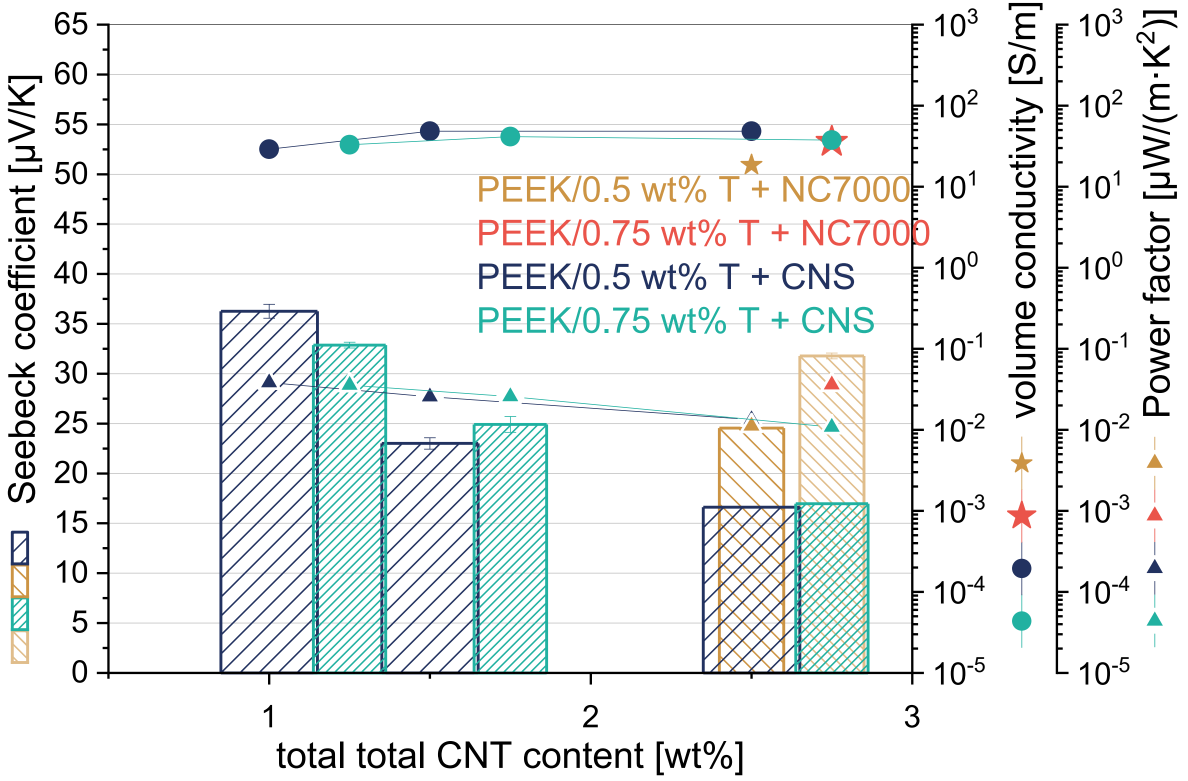
PC = Polycarbonate

Combination effects of polymer and different CNT types: PEEK

One kind of CNT



Hybrid CNT fillers



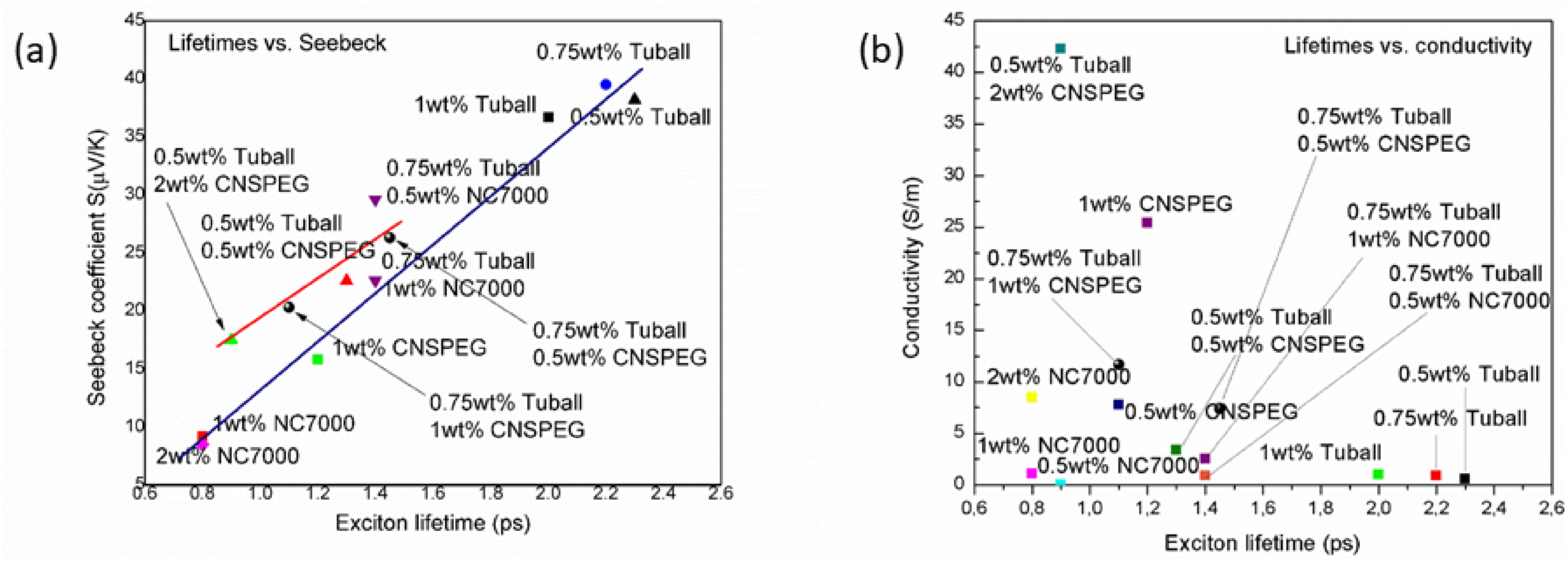
- Highest S-value for PEEK/Tuball
- Highest conductivity for PEEK/CNS

- All thermoelectric parameters are lower compared to single filler composites

I. Konidakis, B. Krause, G.-H. Park, N. Pulumati, H. Reith, P. Pötschke, E. Stratakis, **ACS Applied Energy Materials** 2022, 5, 9770−9781.
PEEK = Polyetheretherketone

Relation between TAS study and thermoelectric results

FOUNDATION FOR RESEARCH AND TECHNOLOGY - HELLAS



- Linear correlation between Seebeck coefficient and exciton lifetime for single filler and mixed filler composites
- No relation between *conductivity* and excition *lifetime*

I. Konidakis, B. Krause, G.-H. Park, N. Pulumati, H. Reith, P. Pötschke, E. Stratakis, **ACS Applied Energy Materials** 2022, 5, 9770−9781.
TAS = ultrafast laser time-resolved transient absorption spectroscopy

Hall measurement on PC composites

- What are the charge carriers doing in mixed filler systems?

Sample	Hall coefficient A_h (cm^3 C^{-1})	charge carrier concentration n (10^{17} cm^{-3})	mobility μ (cm^2 V^{-1} s^{-1})	Conductivity (S/m)
PC+ 1 wt% NC7000	25.3 ± 2.2	2.5 ± 0.2	0.41 ± 0.06	1.1
PC+ 1 wt% CNS-PEG	1.4 ± 0.6	43.6 ± 20.5	0.45 ± 0.21	25.4
PC+ 1 wt% Tuball	43.6 ± 2.9	1.5 ± 0.1	0.35 ± 0.05	1.0
PC+ 0.5 wt% Tuball + 0.5 wt% CNS-PEG	4.7 ± 0.3	13.2 ± 0.1	0.19 ± 0.03	0.7

- Correlation between charge carrier concentration and conductivity
- **Mobility** of carriers is significantly **decreased** in hybrid filler composites compared to single filler composites

I. Konidakis, B. Krause, G.-H. Park, N. Pulumati, H. Reith, P. Pötschke, E. Stratakis, **ACS Applied Energy Materials** 2022, 5, 9770−9781.

General results for polymer/CNT composites

- Typically, industrial CNTs have positive Seebeck coefficient
- Polymer/MWCNT composites have always positive Seebeck coefficient
- Polymer matrix influences the thermoelectric properties of the CNT itself (p- or n-doping)
- Combination of two kind of CNTs in polymer matrix leads to lower thermoelectric performance

- **Possibilities to achieve n-type composites:**

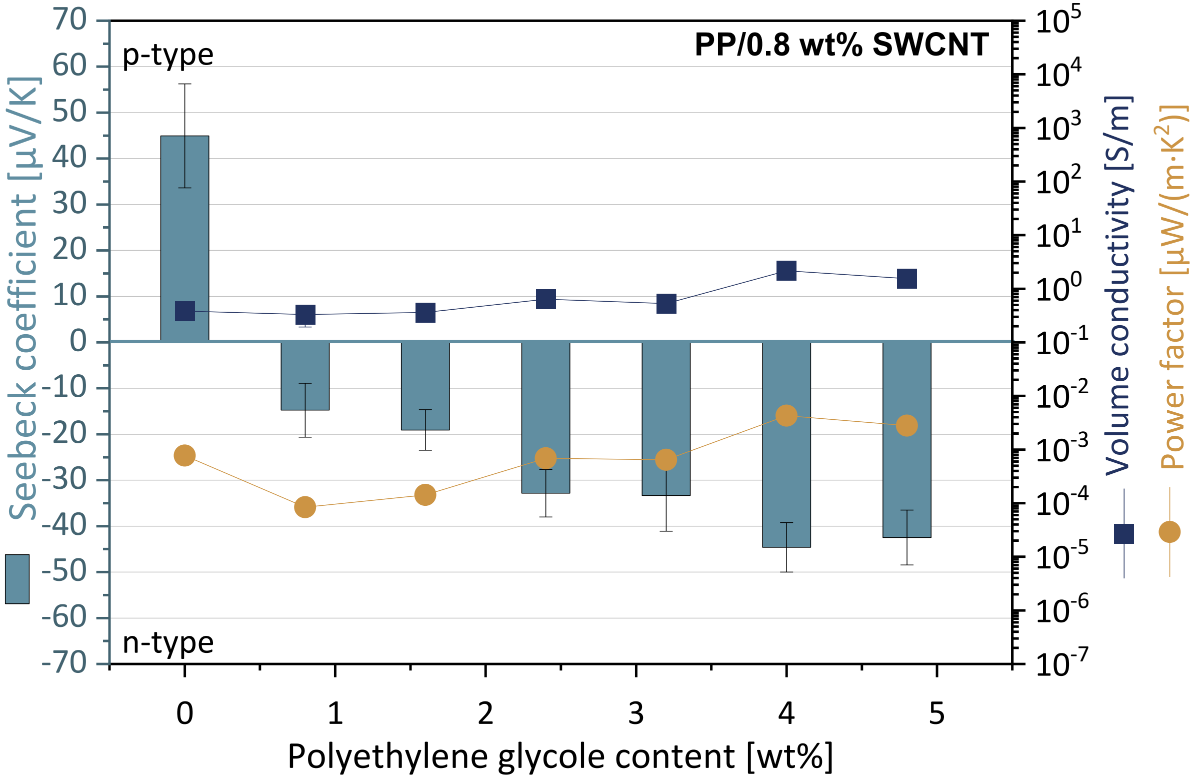
→ Nitrogen doped MWCNT for incorporation in polymer matrix

→ Nitrogen containing matrix polymers in combination with SWCNT

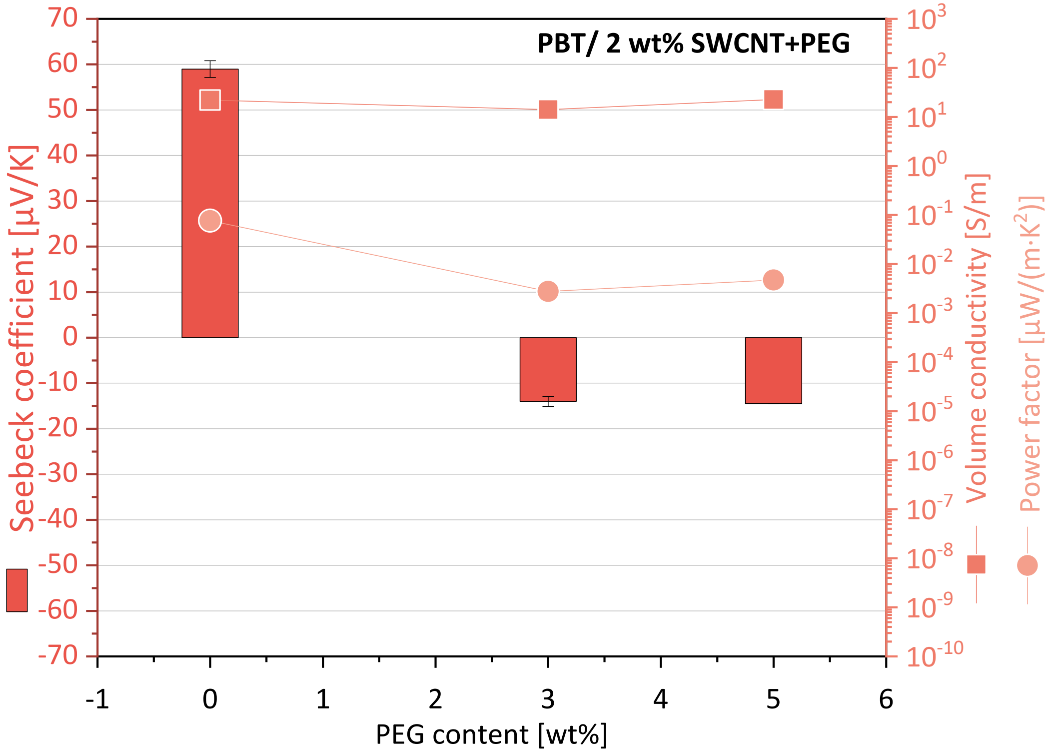
→ Use of switching additives

Use of additives to achieve n-type composites: PP, PBT and PEG

PP



PBT



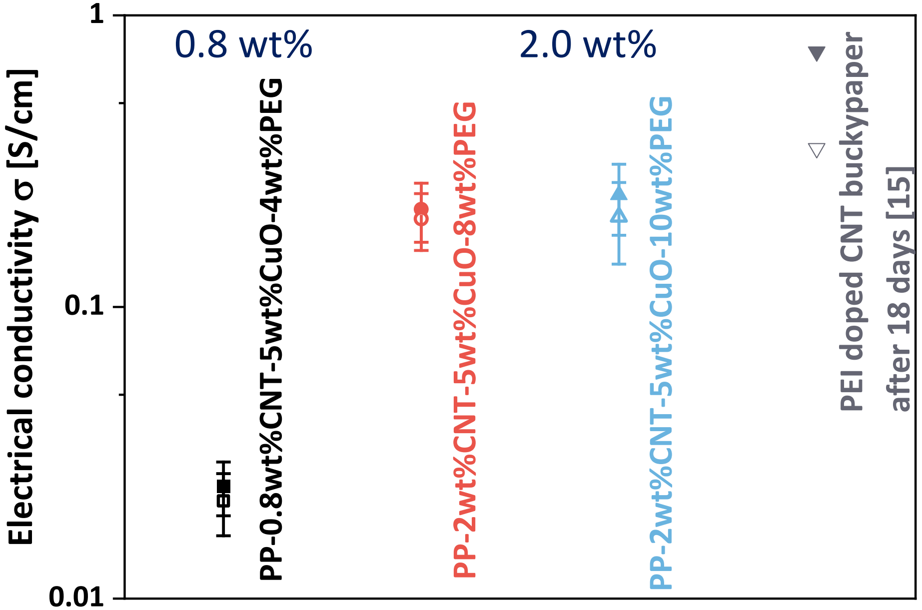
- By addition of **poly ethylene glycole (PEG)** to polymer /SWCNT composites negative Seebeck coefficient values can be reached

J. Luo, G. Cerretti, B. Krause, L. Zhang, T. Otto, W. Jenschke, M. Ullrich, W. Tremel, B. Voit, P. Pötschke, Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol Polymer 2017, 108, 513-520; B.Krause, P. Pötschke, Nanomaterials 2022, 12(21), 3812

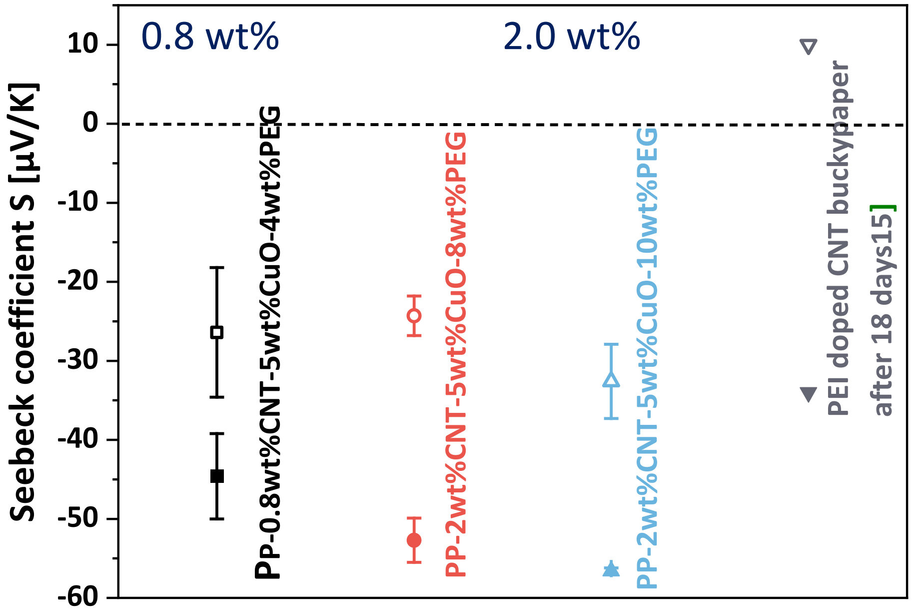
Use of addivites to achieve n-type composites: PP and PEG

Melt processed polymer composites – stability of n-type behaviour (closed symbols before and open symbols after 8 months exposure in air)

Electrical conductivity



Seebeck coefficient

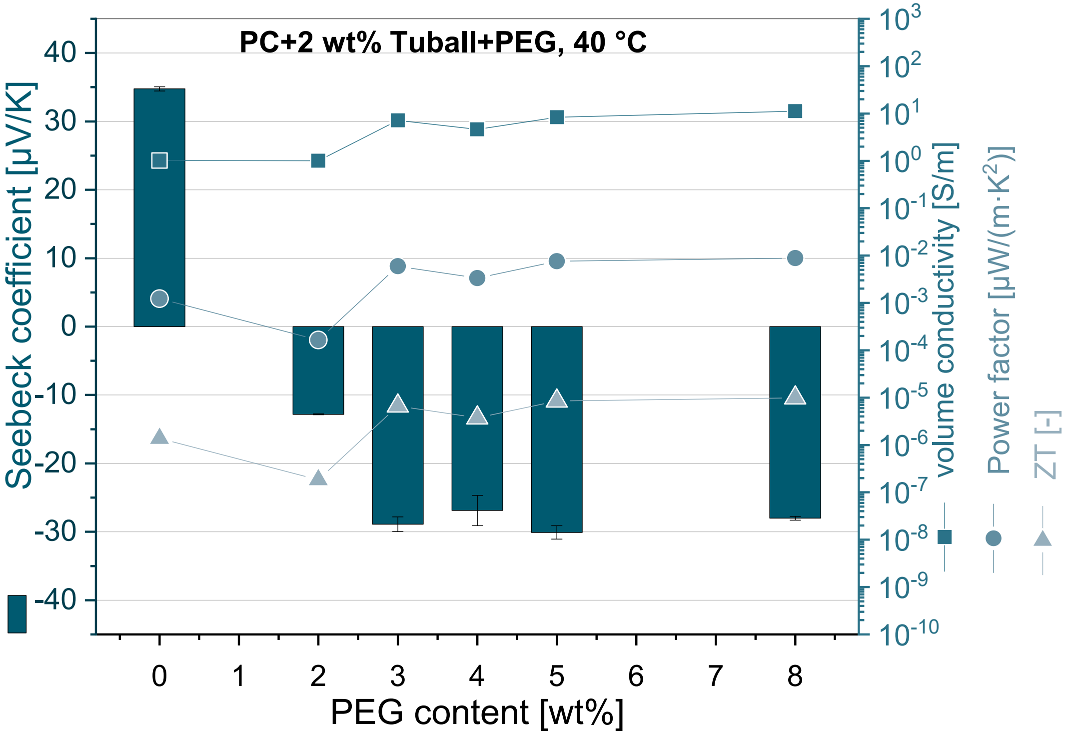


- Stable even after 8 months of storage in air (only slight increase, but still negative)

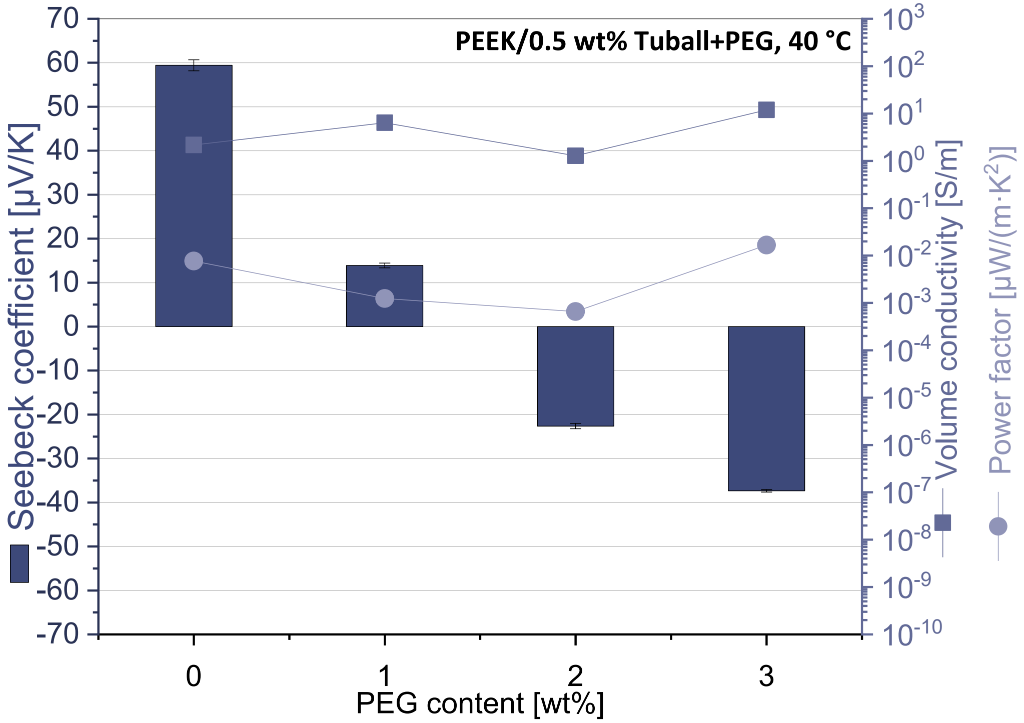
J. Luo, G. Cerretti, B. Krause, L. Zhang, T. Otto, W. Jenschke, M. Ullrich, W. Tremel, B. Voit, P. Pötschke, Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol, Polymer, 2017, 108, 513-520

Use of addivites to archieve n-type composites: PC,PEEK and PEG

PC



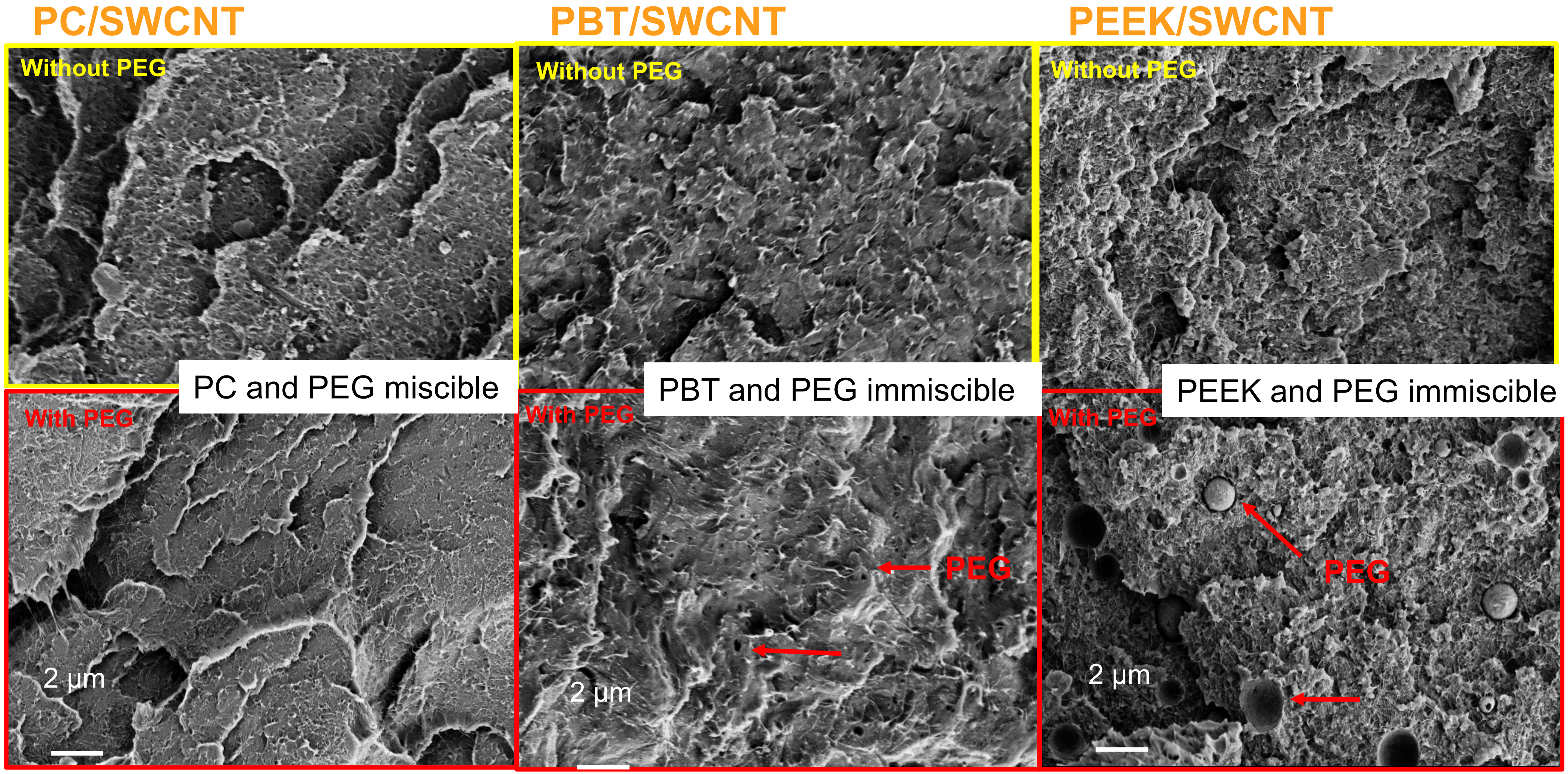
PEEK



- By addition of **poly ethylene glycole (PEG**) to polymer /SWCNT composites negative Seebeck coefficient values can be reached

B. Krause, P. Pötschke, Nanomaterials 2022, 12(21), 3812

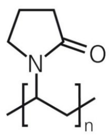
Use of addivites to achieve n-type composites: Miscibility with PEG



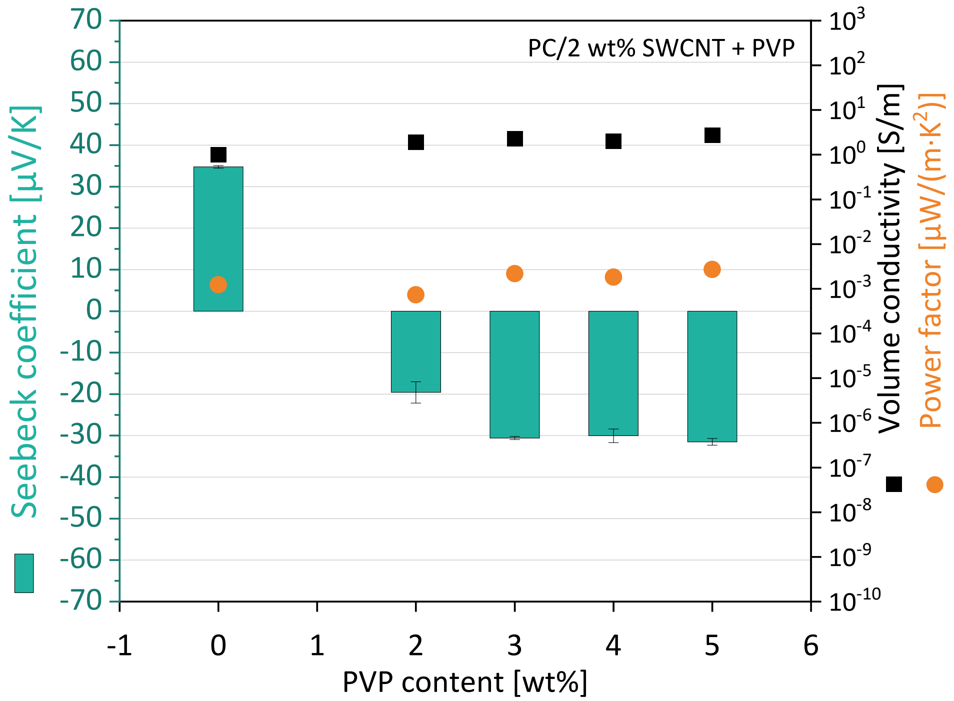
PEG = Polyethylene glycol
SEM images on cryo-fractured surfaces

B.Krause, P. Pötschke, Nanomaterials 2022, 12(21), 3812

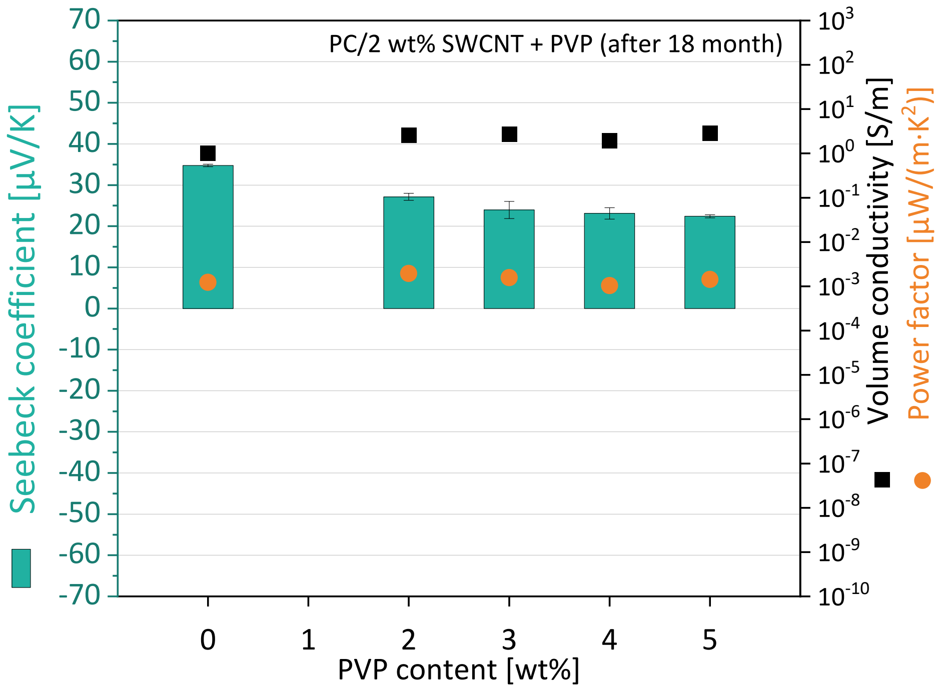
Use of addivites to achieve n-type composites:PC and PVP



PC/SWCNT+PVP (0 month)



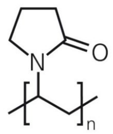
PC/SWCNT+PVP (after 18 month)



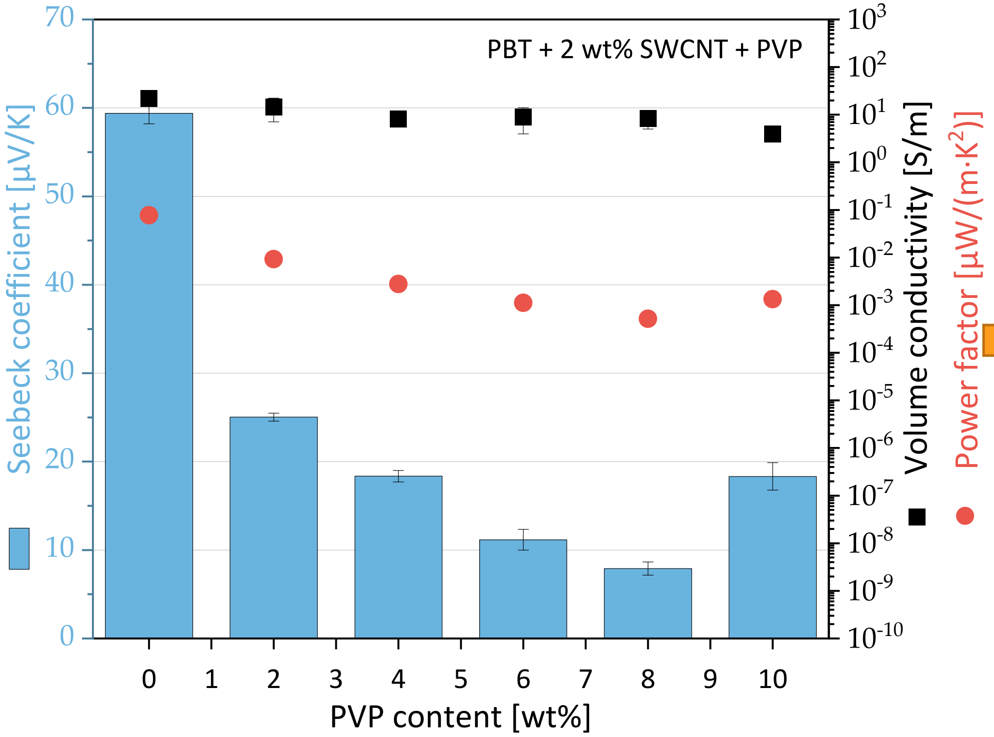
- By addition of **polyvinylpyrrolidone (PVP**) to PC/SWCNT composites negative Seebeck coefficient values can be reached, but this sign is not long term stable

B. Krause, S. Imhoff, B. Voit, P. Pötschke, **micromachines 2023**, 14(1), 181

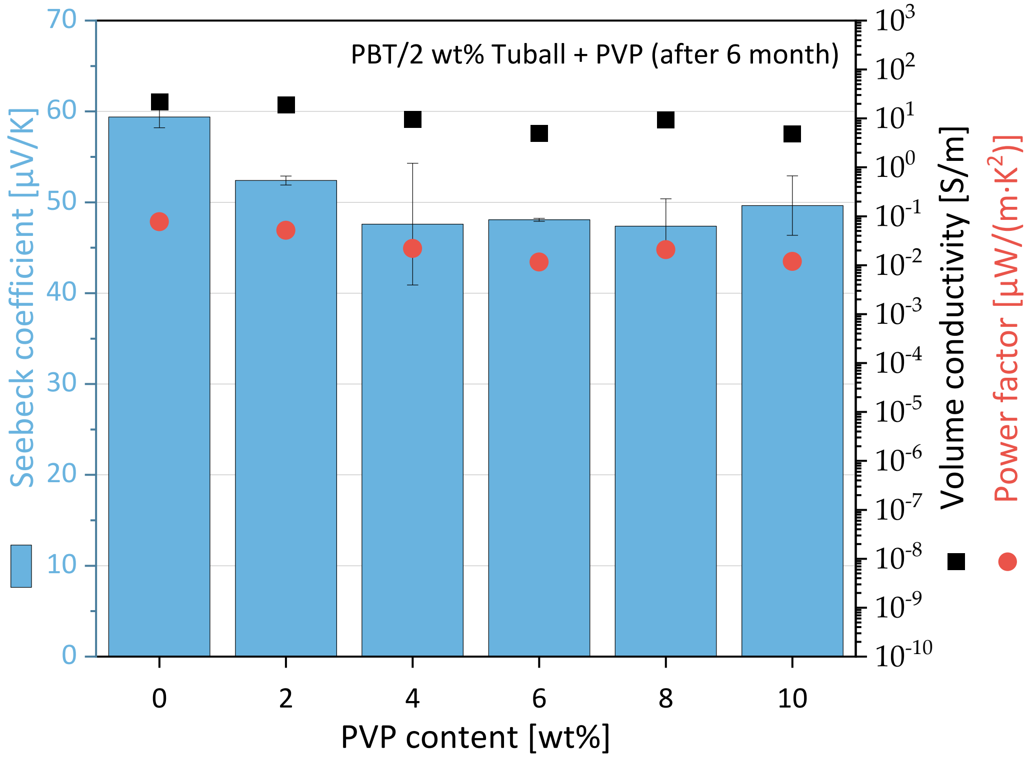
Use of addivites to achieve n-type composites: PBT and PVP



PBT/SWCNT+PVP (0 month)



PBT/SWCNT+PVP (after 6 month)

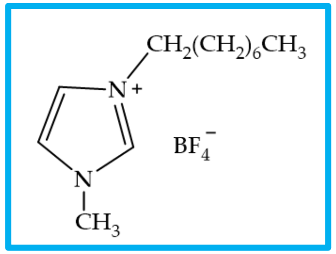


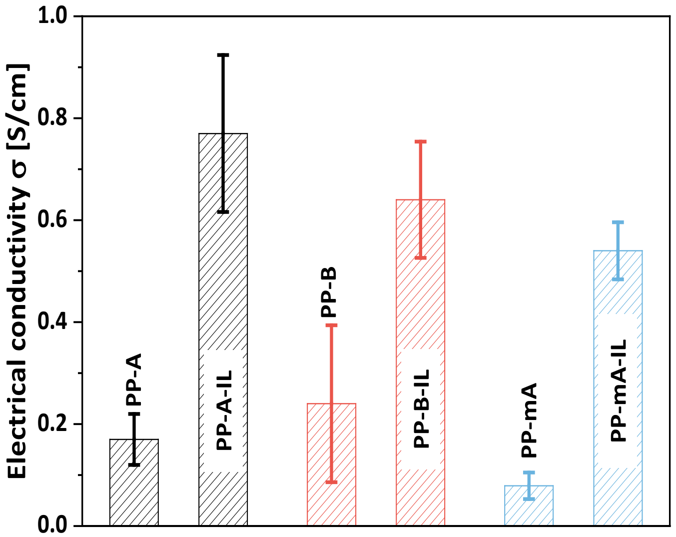
- By addition of **polyvinylpyrrolidone (PVP)** to PBT/SWCNT composites negative Seebeck coefficient values can be reached, but this sign is not long term stable

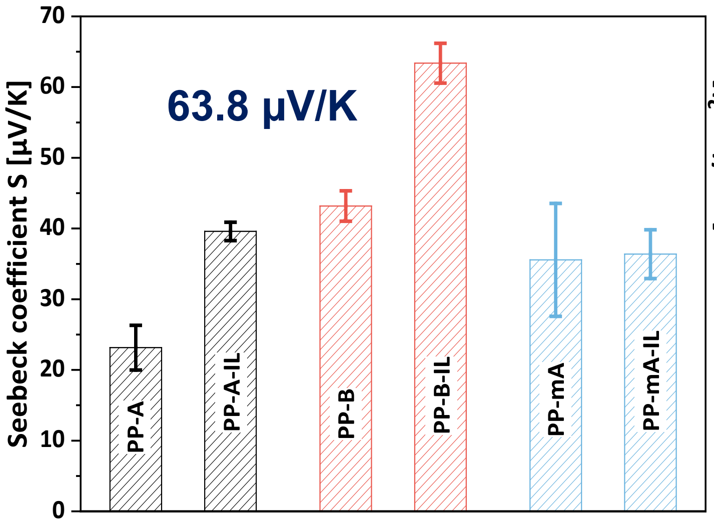
B.Krause, S. Imhoff, B. Voit, P. Pötschke, **micromachines 2023**, 14(1), 181

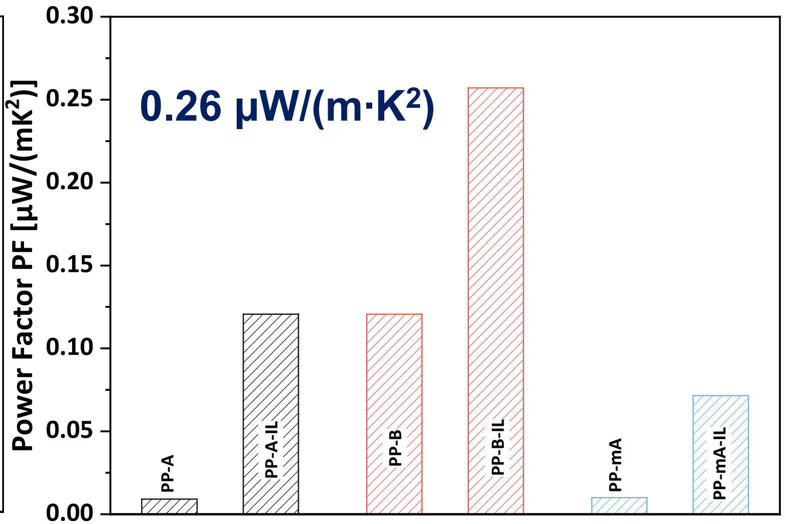
Use of additives to achieve n-type composites: PP and ionic liquids

ionic liquid (IL) 1-methyl-3-octylimidazolium tetrafluoroborate (OMIM BF4)

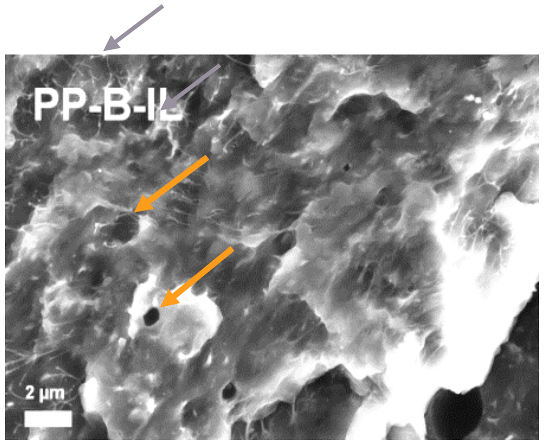








- Different kinds of SWCNT were studied
- IL increase the electrical conductivity and TE parameters of composites filled with all three types of SWCNT
- Effect on TE properties occurs although PP and IL are immiscible



Holes of IL visible (SEM of cryo-fractured surface)

J. Luo, B. Krause, P. Pötschke, Polymer Carbon Nanotube Composites for Thermoelectric Applications, Polymer Carbon Nanotube Composites for Thermoelectric Applications, **AIP Conference Proceedings 2017**, 1914, 030001.

Use of additives to achieve n-type composites: PP and ionic liquid

PP/SWCNT+IL composites: Influence of melt processing conditions

Material	Electrical conductivity [S/cm]	Seebeck coefficient [µV/K]	Power Factor [µW/mK^2]
PP-CNT-IL-250rpm-210C-5min	**0.54**	36.4	0.072
PP-CNT-IL-250rpm-230C-5min	**0.54**	36.7	0.073
PP-CNT-IL-100rpm-210C-5min	0.47	**45.6**	**0.098**
PP-CNT-IL-100rpm-230C-5min	0.41	42.2	0.073

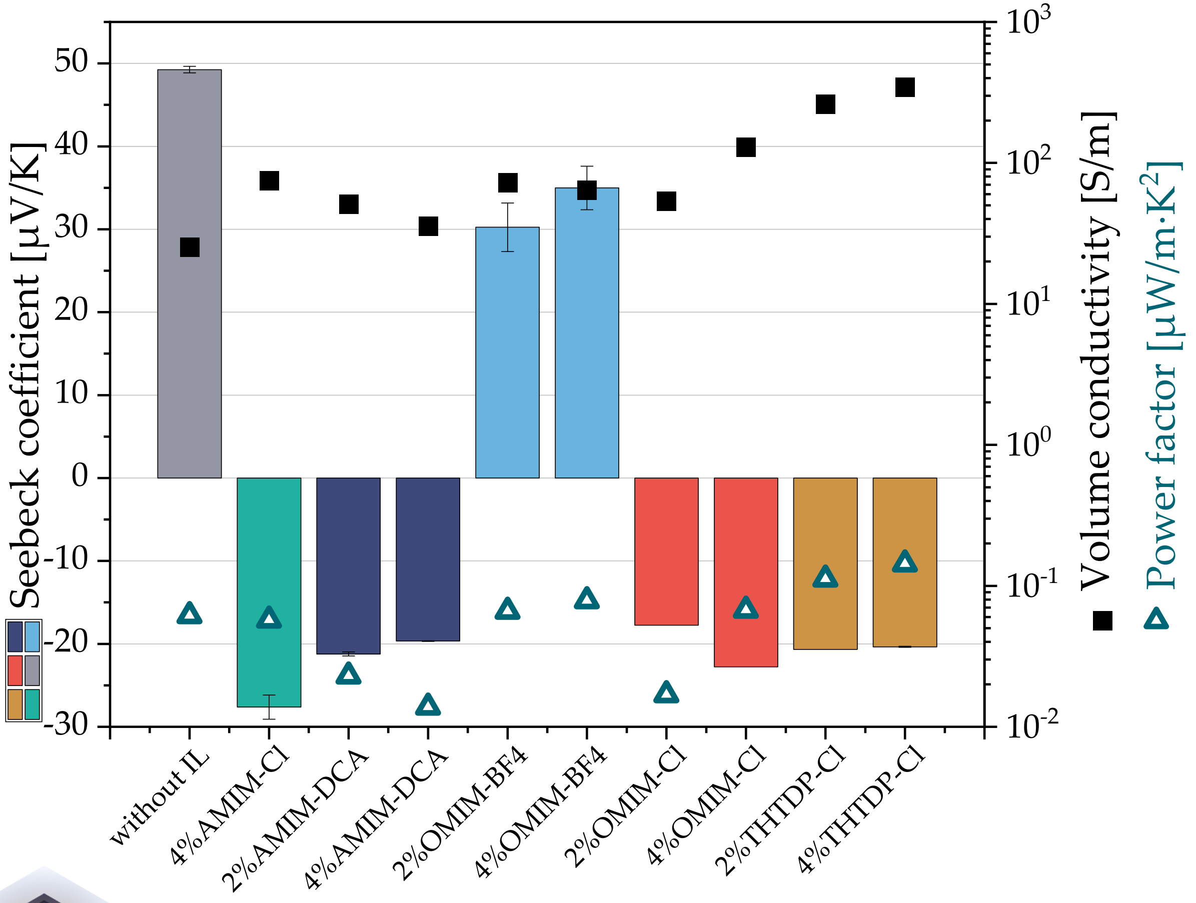
- **Lower shear stress at smaller rotation speed → higher Seebeck coefficient**
- Only small influence of melt mixing conditions on thermoelectric properties

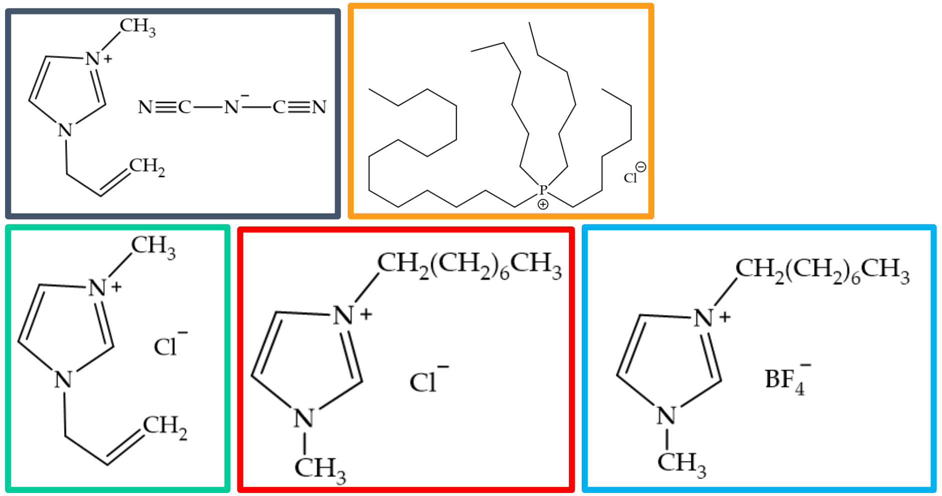
J. Luo, B. Krause, P. Pötschke, Polymer Carbon Nanotube Composites for Thermoelectric Applications, Polymer Carbon Nanotube Composites for Thermoelectric Applications, **AIP Conference Proceedings 2017**, 1914, 030001.

Use of addivites to generate n-type composites

Switching strongly depends on molecular structure of ionic liquid (IL) and its anion

PP/2 wt% SWCNT+IL





- Effect on TE properties occurs although PP and IL are immiscible, expect THTDP Cl

1-allyl-3-methyl-imidazolium chloride (AMIM Cl)
1-methyl-3-octylimidazolium tetrafluoroborate (OMIM BF4)
1-methyl-3-octylimidazolium chloride (OMIM Cl)
1-allyl-3-methylimidazolium dicyanamide (AMIM DCA)
Trihexyltetradecylphosphonium chloride (THTDP Cl)

O. Voigt, B. Krause, P. Pötschke, M. T. Müller, S. Wießner, **Journal of Compoosites Science 2022**, 6(1), 25.

General results for polymer/CNT composites with n-type behaviour

- **Possibilities to achieve n-type materials:**

→ Use of additives to pretreat CNTs for incorporation in polymer matrix

- *Polyethylene glycol (PEG)*
  - Suitable in PP, PC, PBT, PEEK
  - Long term stable
- *Polyvinylpyrrolidone (PVP)*
  - Suitable in PC, PBT
  - BUT not long term stable
- *Ionic liquids (ILs)*
  - Suitable in PP
  - Strongly depending on molecular structure and IL anion

Combination effects of cellulose and CNT types

Cellulose films and aerogels + CNTs

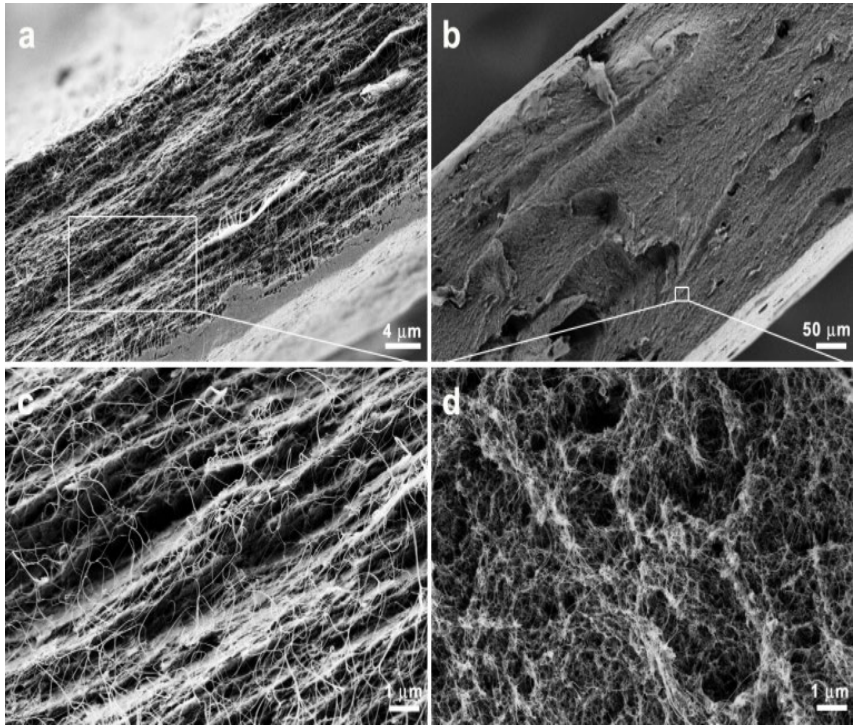
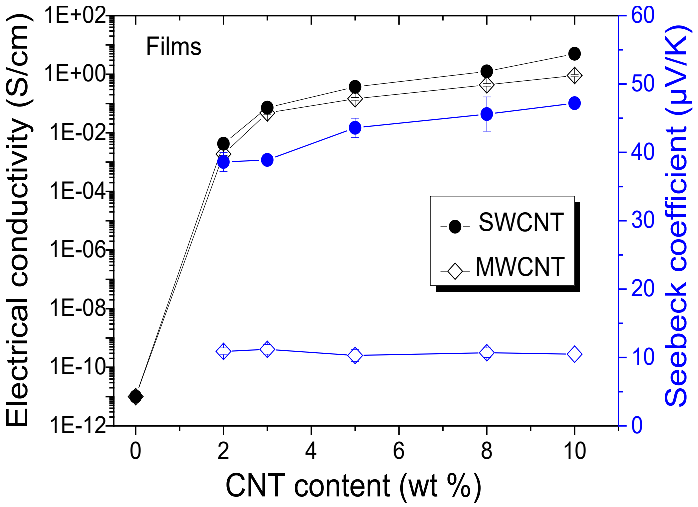
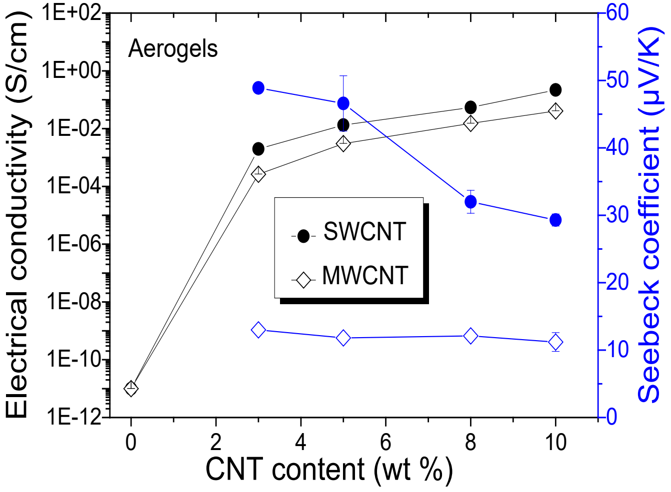


Figure 3. SEM images of the cross-section of cellulose/SWCNT nanocomposite (5 wt% SWCNT): (a) and (c) solid film; (b) and (d) aerogel.





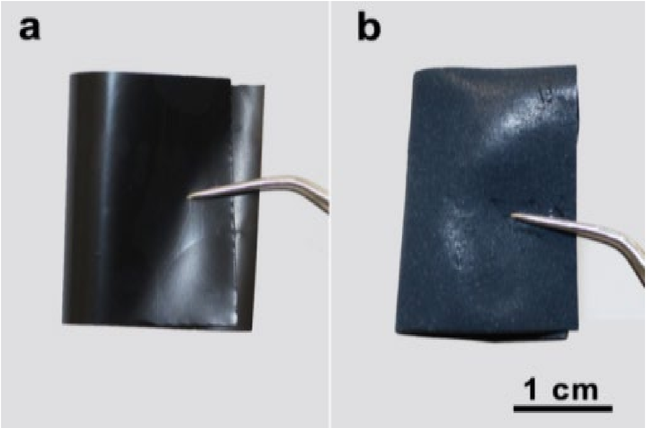


Figure 2. Photographs of flexible cellulose/SWCNT nanocomposites (5 wt% SWCNT): (a) solid film; (b) aerogel.

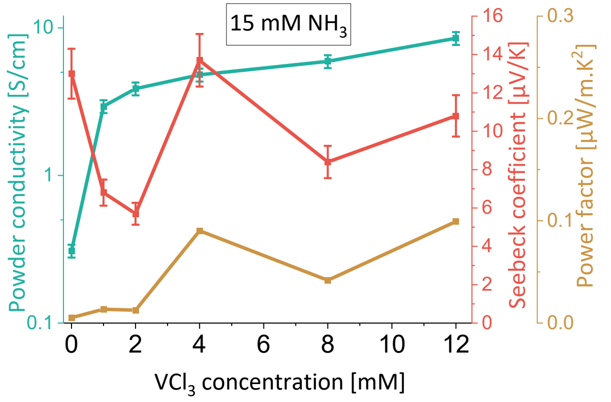
PF 1.1 µW/(m·K²)
@ 10 wt% SWCNTs
in films

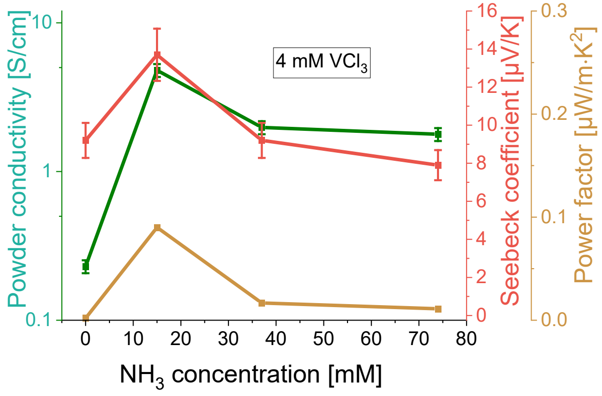
M. Gnanaseelan, Y. Chen, J. Luo, B. Krause, P. Pötschke, J. Pionteck, H. Qi, Cellulose-carbon nanotube composite aerogels as novel thermoelectric materials, **Comp Sci Techn 2018**, 163, 133-140

Combination effects of SBS and reduced GO types

VCl_3 assisted reduction of graphite oxide (GO) and solution prepared SBS composites

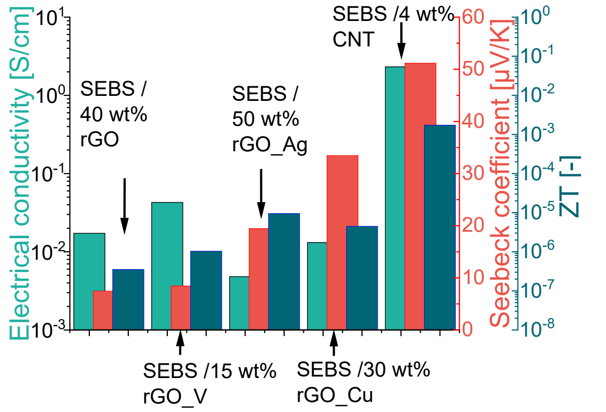
Synthesis of rGO by hydrothermal reduction in presence of metal salts



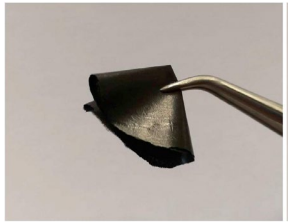


- Highest Seebeck coefficient of rGO = 14 µV/K
- Highest Seebeck coefficient of SBS/rGO = 34 µV/K
- Even higher Seebeck coefficient of SBS/4 wt% SWCNT = 51.2 µV/K
- Highest PF = 0.6 µW/(m·K²), highest ZT = 0.0017

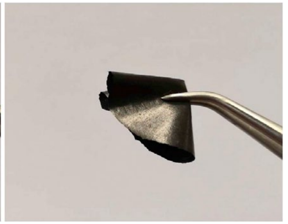
SBS composites with rGO in different filler levels



SBS/30 wt% rGO



SBS/30 wt% rGO_VCl_3

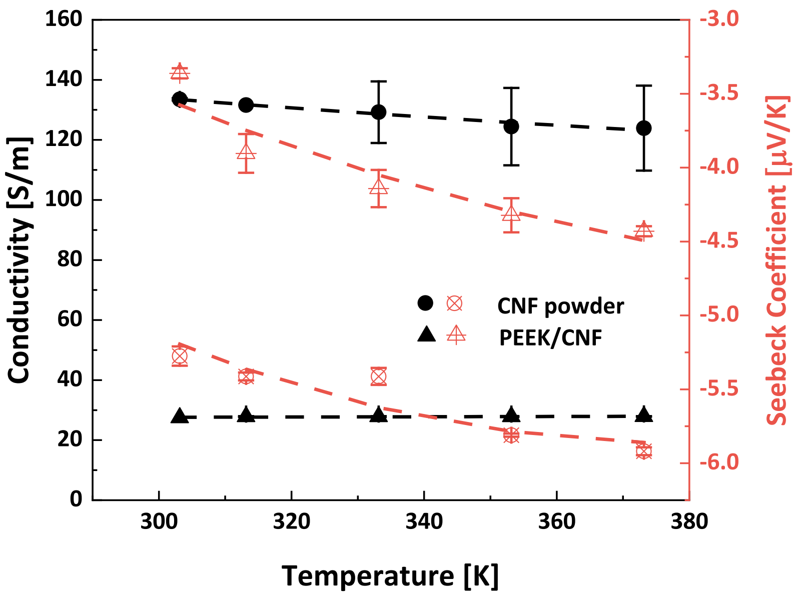


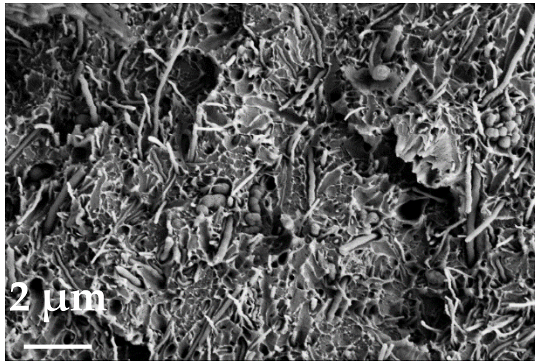
M. Gnanaseelan, S. Samanta, J. Pionteck, D. Jehnichen, F.Simon, P. Pötschke, B. Voit, **Materials Chemistry and Physics 2019,** 229, 319–329

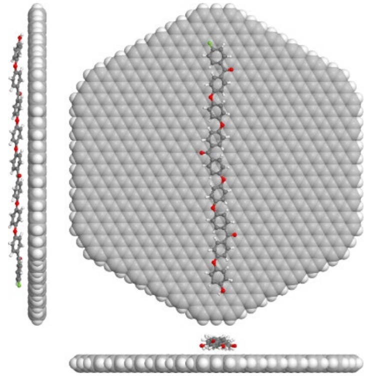
SBS = poly (styrol-butadien-styrol) copolymer, VCl_3 = vanadium(III)-chloride, rGO = reduced graphene oxide

Combination effects of polymer and carbon nanofibres (CNF)

PEEK composites with carbon nanofibres (Pyrograf® III PR 24 LHT XT)







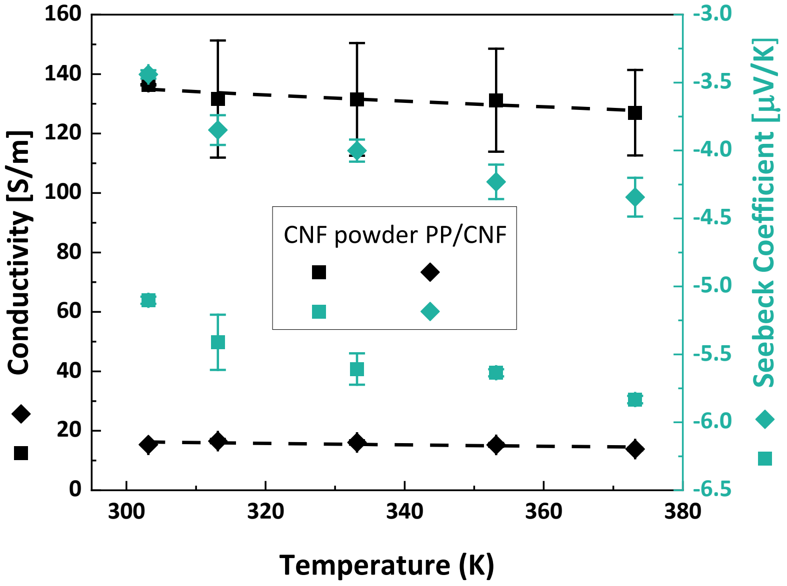
- Seebeck coefficient of composites is higher than the pure CNF powder
- → p-doping of PEEK on CNF occurs

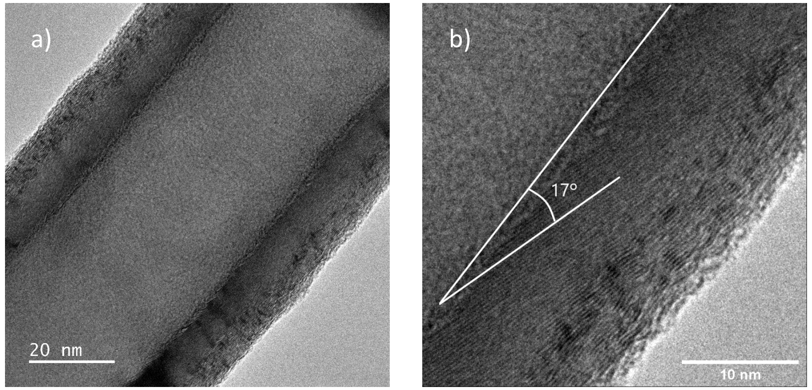
- N-type thermoelectric behaviour of CNF leads to n-type PEEK composite
- With increasing temperature the n-type behaviour is more pronounced

A. J. Paleo, B. Krause, D. Soares, M. Melle-Franco, E. Muñoz, P. Pötschke, A. M. Rocha, Thermoelectric properties of n-type poly(ether ether ketone) carbon nanofiber melt-processed composites, **Polymers 2022**, 14, 4803.

Combination effects of polymer and carbon nanofibres (CNF)

PP composites with carbon nanofibres (Pyrograf®-III PR 19 LHT XT)





TEM images of CNF

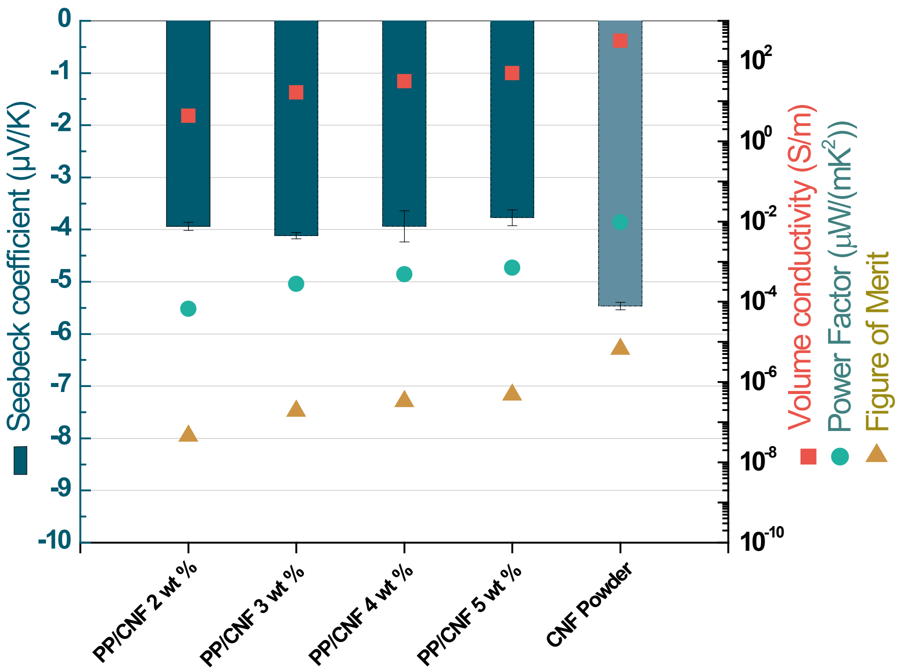
- Seebeck coefficient of composites is higher than the pure CNF powder
- → p-doping of PP on CNF occurs

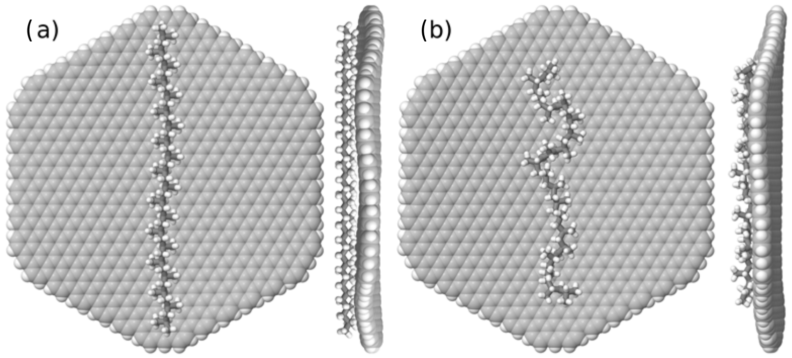
- N-type thermoelectric behaviour of CNF leads to n-type PP composite
- With increasing temperature the n-type behaviour is more pronounced

Antonio J. Paleo, Beate Krause, Maria F. Cerqueira, Enrique Muñoz, Petra Pötschke, Ana M. Rocha, Nonlinear Thermopower Behaviour of N-Type Carbon Nanofibres and Their Melt Mixed Polypropylene Composites, **polymers 2022**, 14, 269.

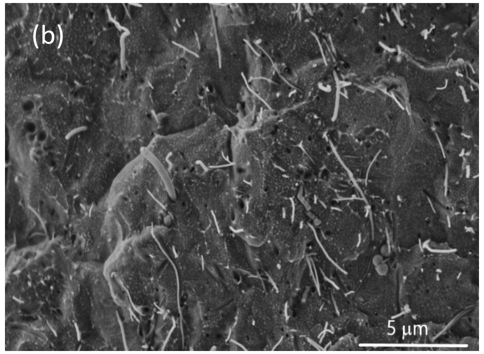
Combination effects of polymer and carbon nanofibres (CNF)

PP composites with carbon nanofibres (Pyrograf® III PR 24 LHT XT)





Molecular geometries of (a) syndiotactic and (b) isotactic polypropylene



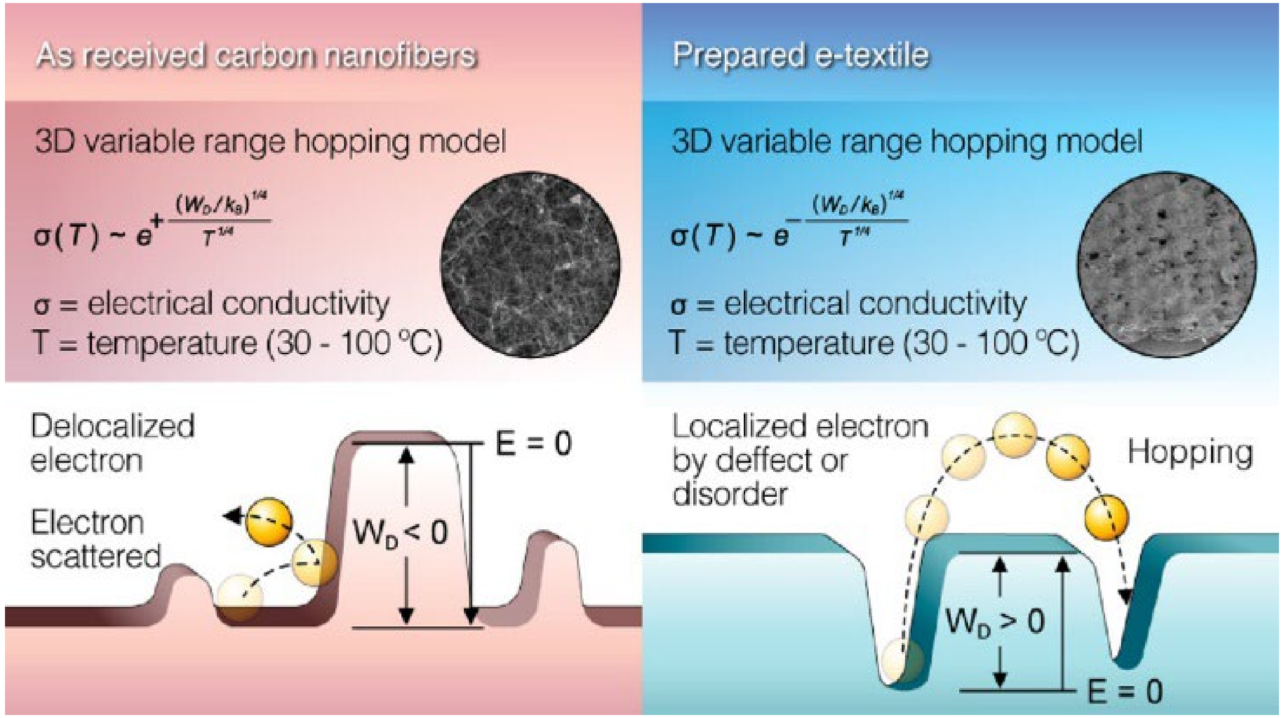
Well dispersed CNF in PP matrix (SEM image on cryofractured surface)

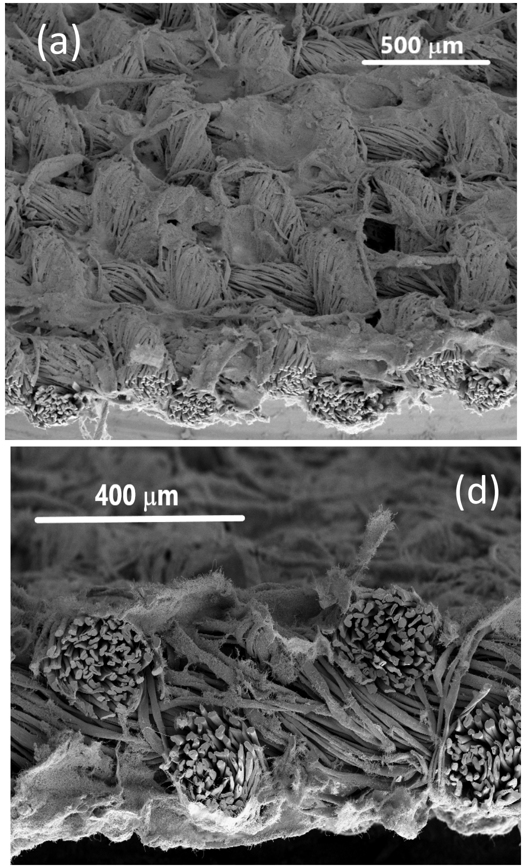
- N-type thermoelectric behaviour of CNF leads to n-type PP composite
- PF and ZT increase with CNF content

A. J. Paleo, B. Krause, M. F. Cerqueira, M. Melle-Franco, P. Pötschke, Ana María Rocha, Thermoelectric properties of polypropylene carbon nanofiber melt-mixed composites: exploring the role of polymer on their Seebeck coefficient, Polymer Journal (2021) 53:1145–1152

Combination effects of cotton and carbon nanofibres (CNF)

Textiles coated with CNF (Pyrograf® III PR 24 LHT XT)





- Cotton woven textiles were functionalised by dip-coating with n-type CNF dispersion to generate n-type e-textiles

A. J. Paleo, B. Krause, M. F. Cerqueira, E. Muñoz, P. Pötschke, A. M. Rocha, Electronic Features of Cotton Fabric e-Textiles Prepared with Aqueous Carbon Nanofiber Inks, ***ACS Appl. Eng. Mater.* 2023**, 1, 1, 122-131

General results for polymer/CNF composites

- Incorporation of n-type CNF in polymers leads to n-type composites
  → Suitable for PP and PEEK

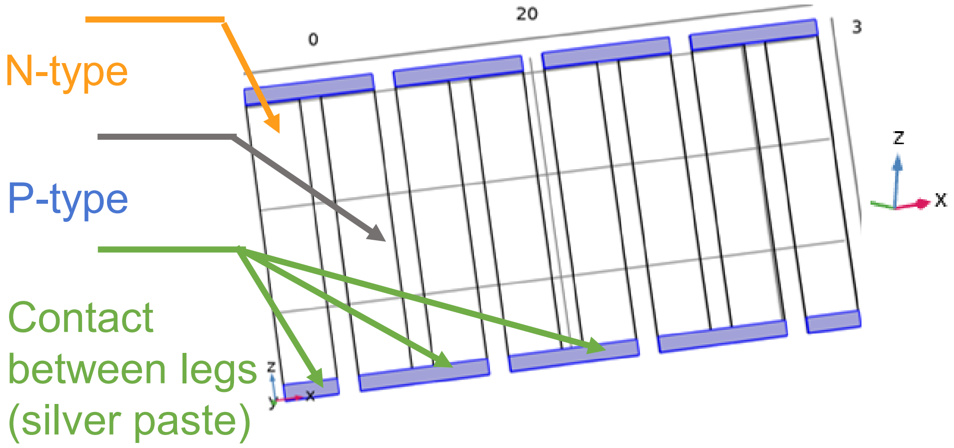
- PP and PEEK have a p-doping effect on CNFs that is comparable to their effect on CNTs

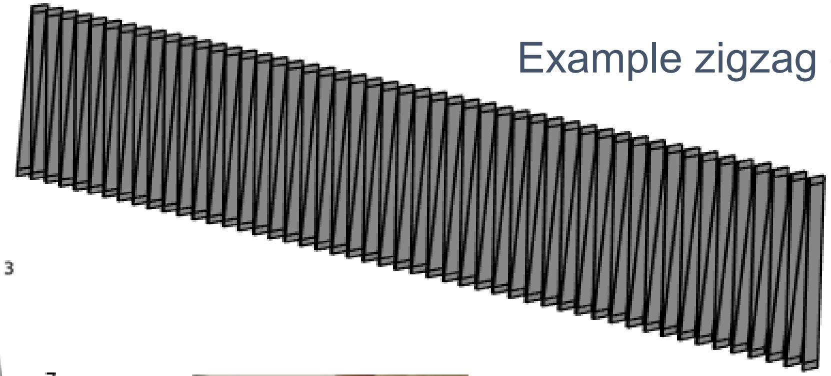
- Dip-coating of cotton textile with n-type CNF dispersion leads to n-type textiles

Prototype modules for thermoelectric generators (TEG)

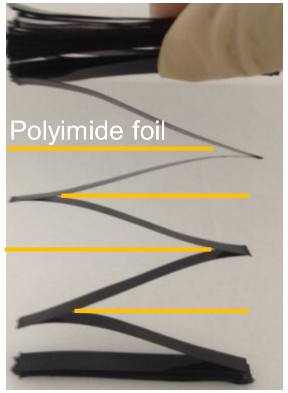
Polymer properties such as flexibility and free shapeability enable different designs than metal-based TEGs

Example planar design





Example zigzag design

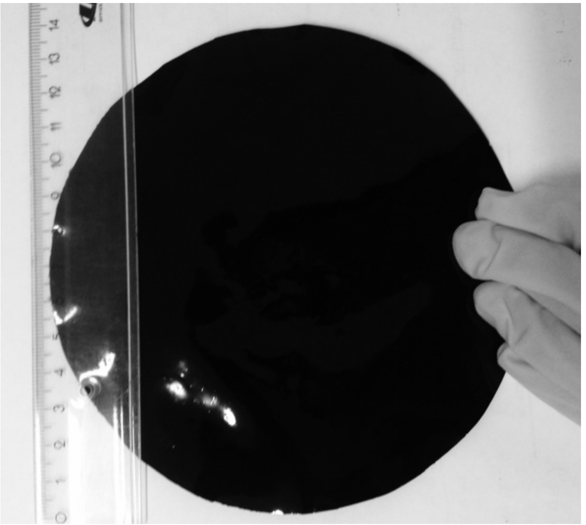


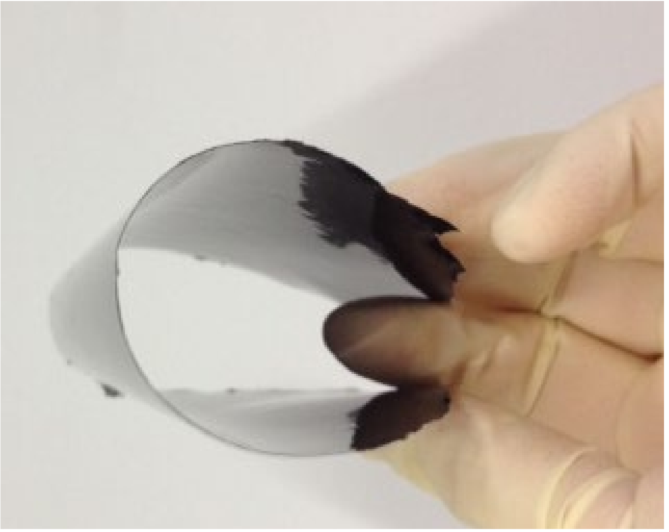
Q. Doraghi, A. Żabnieńska-Góra, L. Norman, B. Krause, P. Pötschke, H. Jouhara, Experimental and computational analysis of thermoelectric modules based on melt-mixed polypropylene composites, **Thermal Science and Engineering Progress 2023**, 39, 101693

Prototype modules for thermoelectric generators

Melt processed polymer composites

p- and n-type needed
p-type: PP+2 wt% SWCNTs + 5 wt% CuO
n-type: PP+2 wt% SWCNTs + 5 wt% CuO + 10 wt% PEG





Modules:

- Planar type: module 1
- with 4 thermocouples
- (4 layers of p-type and 4 layers of n-type)

- Vertical type: module 2
- with 49 thermocouples
- (49 layers of p-type and 49 layers of n-type)

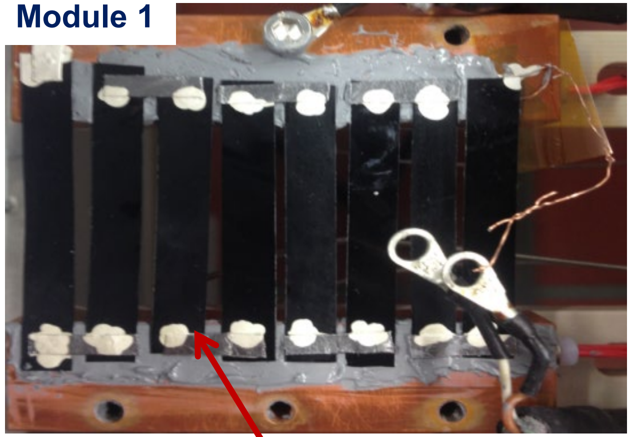
J. Luo, G. Cerretti, B. Krause, L. Zhang, T. Otto, W. Jenschke, M. Ullrich, W. Tremel, B. Voit, P. Pötschke, Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol, Polymer, 2017, 108, 513-520

Prototype modules for thermoelectric generators

Melt processed polymer composites

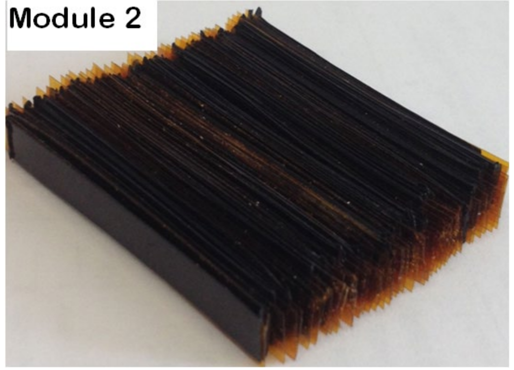
p-type: PP +2 wt% SWCNT +5wt% CuO
n-type: PP+ 2wt% SWCNT+5 wt% CuO+10 wt% PEG

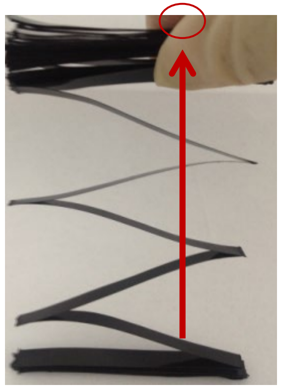
Module 1



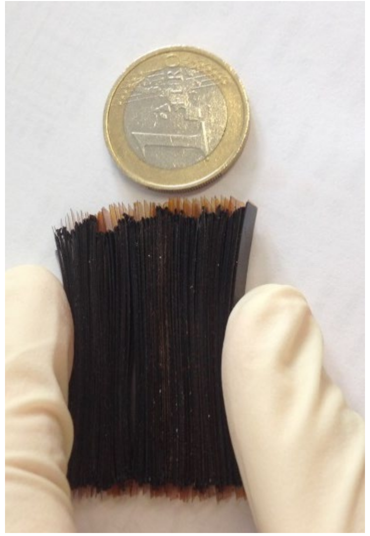
For module 1 (planar type):
4 thermocouples
connections were made by silver paste and graphite foil

Module 2





accordion like structure

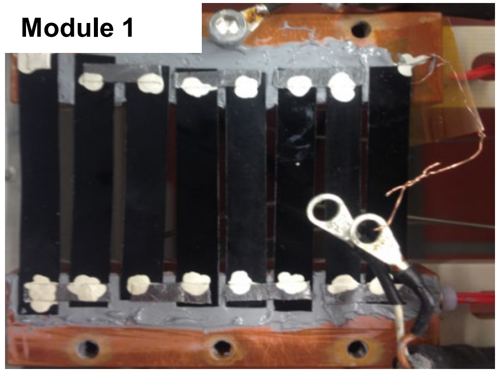


For module 2 (vertical type):
49 thermocouples
connections were made by pressing films at 110°C (slightly below T_m of PP)

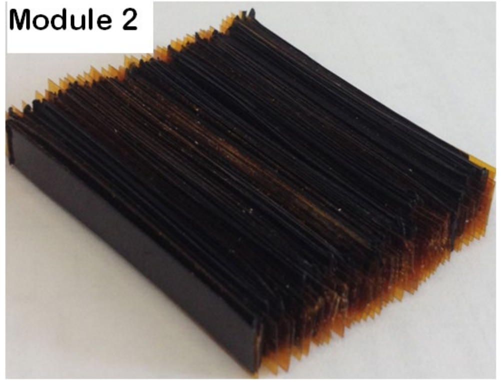
J. Luo, G. Cerretti, B. Krause, L. Zhang, T. Otto, W. Jenschke, M. Ullrich, W. Tremel, B. Voit, P. Pötschke, Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol, Polymer, 2017, 108, 513-520

Prototype modules for TEG thermoelectric generators

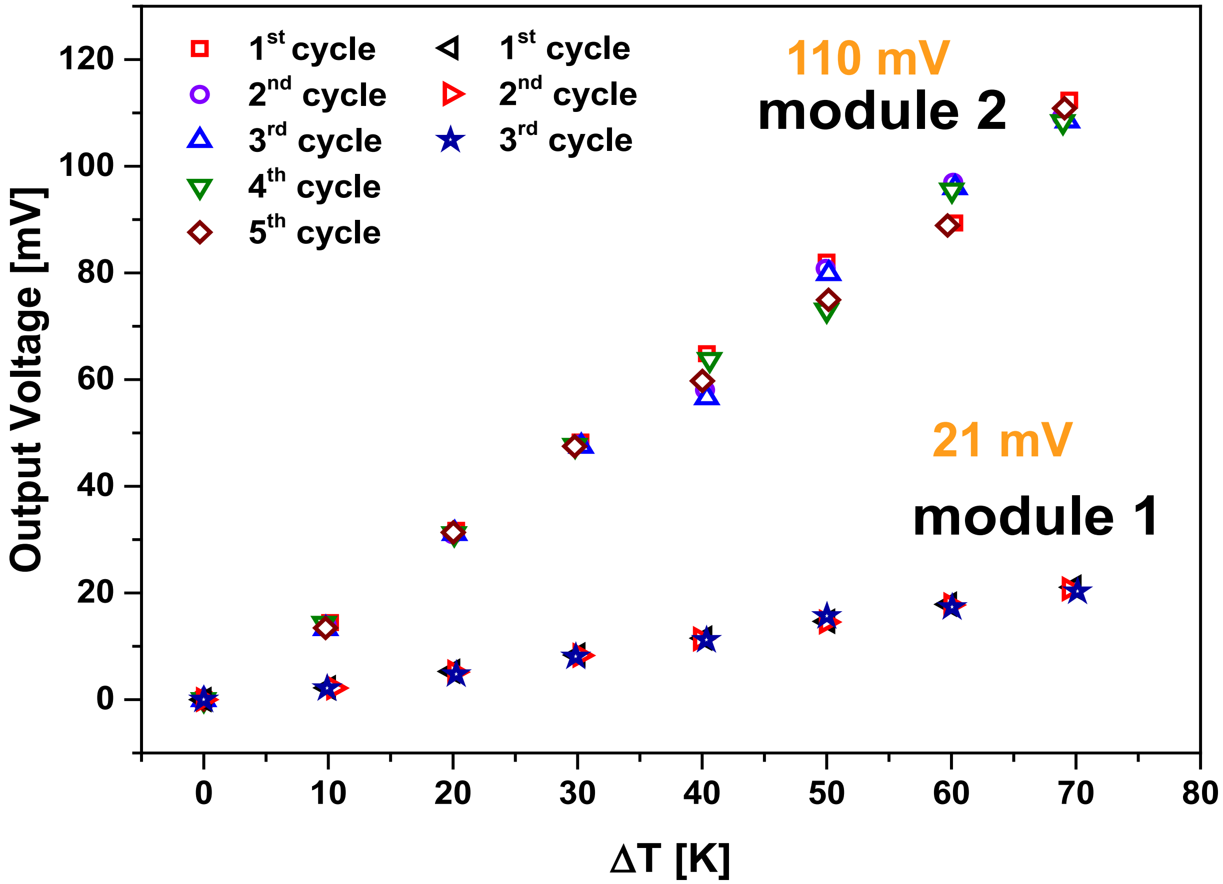
Melt processed polymer composites



4 thermocouples



49 thermocouples

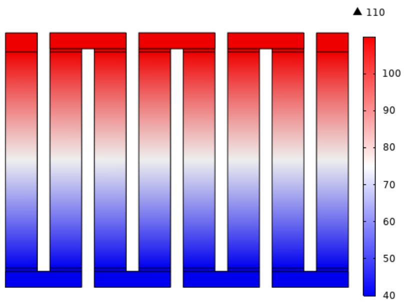


J. Luo, G. Cerretti, B. Krause, L. Zhang, T. Otto, W. Jenschke, M. Ullrich, W. Tremel, B. Voit, P. Pötschke, Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol, Polymer, 2017, 108, 513-520

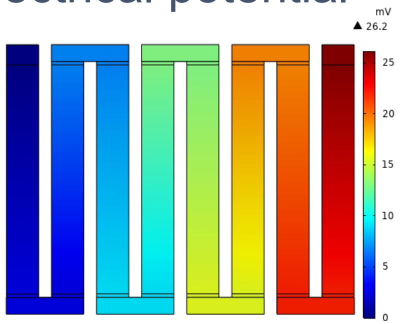
Prototype modules for thermoelectric generators

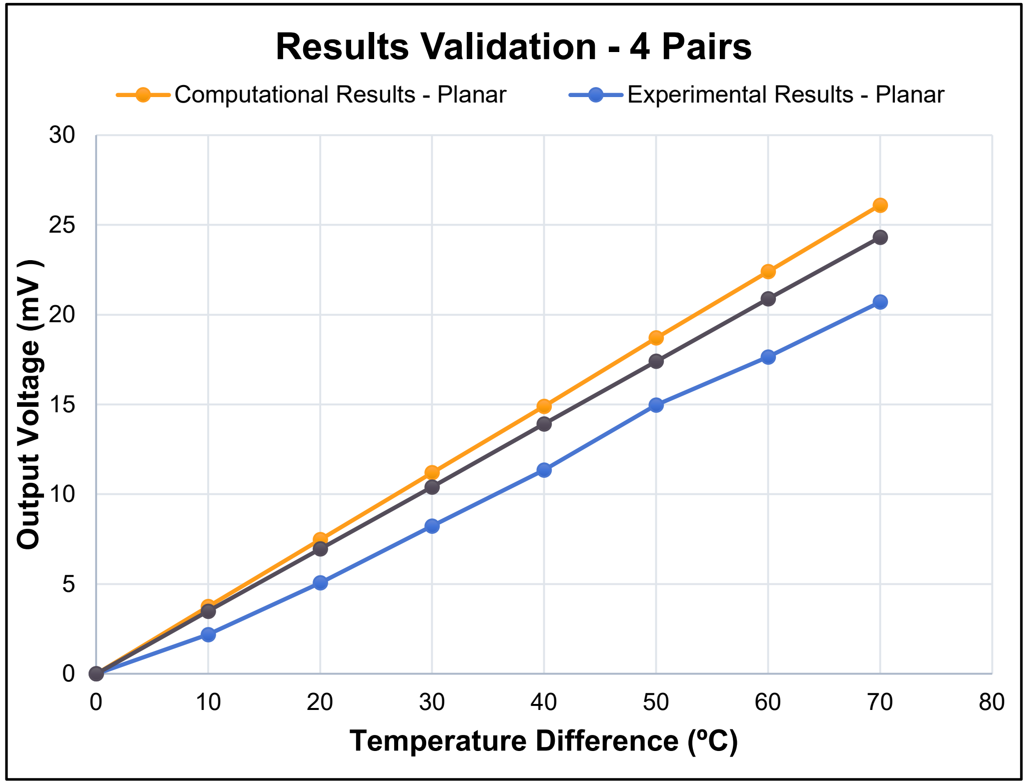
Comparison between Comsol model and experimental results

Temperature distribution



Electrical potential





- Good agreement for 4-pair module whose elements were connected with conductive silver and graphite foil

Q. Doraghi, A. Żabnieńska-Góra, L. Norman, B. Krause, P. Pötschke, H. Jouhara, Experimental and computational analysis of thermoelectric modules based on melt-mixed polypropylene composites, **Thermal Science and Engineering Progress 2023**, 39, 101693

Summary and Outlook

Polymer based TE materials still have much **lower efficiency values than traditional TE materials** (max. ZT in this research $1.6 \cdot 10^{-4}$ vs. ca. 1)

- However, **significant improvements** were done in last years
- Melt mixed composites have lower PF and ZT values than intrinsically conductive polymers (PEDOT:PSS) and solution mixed composites
- Based on the advantages of polymers for T<150°C polymer composites are promising when only low voltages are needed

General tendencies observed on melt mixed composites with CNTs:

- **SWCNTs** result in **better** performance than MWCNTs
- Addition of CuO and IL enhances S and PF
- Best values of this research: p-type: **S 66.8 μV/K, PF 0.26 μW/m·K^2,**
  n-type: **S -59.8 μV/K, PF 0.14 μW/m·K^2**
- **Switching from p-type to n-type** easily possible
- two modules were fabricated to demonstrate melt mixing to fabricate thermoelectric materials and thereby thermoelectric generators (**max. 110 mV so far**)

Publications of IPF on TE materials and modules with carbon nanotubes

- Doraghi et al., Thermal Science and Engineering Progress 2023, 39, 101693 (PP)
- Krause et al., Micromachines 2023, 14(1), 181 (PC, PBT, PEEK)
- Krause et al., Nanomaterials 2022, 12(21), 3812 (PC, PBT, PEEK)
- Konidakis et al., ACS Applied Energy Materials 2022, 5, 9770−9781 (PC, PEEK)
- Voigt et al., Journal of Composites Science 2022, 6(1), 25 (PP)
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- Krause et al., Journal of Composites Science 2020, 4 (1), 14 (PP)
- Krause et al., Energies, 2020, 13(2), 394 (PP)
- Jenschke et al., Technisches Messen 2020, 87(7-8), 495-503 (on TE equipment)
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- Pötschke et al., TechConnect Briefs 2018, 1, 196 – 199 (PP)
- Gnanaseelan et al., Composites Science and Technology, 2018, 163, 133-140 (cellulose)
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- Gonçalves et al, Polymers 2018, 10 (8), 925 (PEEK)

Publications of IPF on TE materials and modules with carbon nanotubes

- Luo et al., AIP Conference Proceedings 1914 (2017), 030001 (PP)
- Luo et al., Polymer, 2017, 108, 513-520 (PP)
- Luo et al., AIMS Materials Science, 3(2016) 3, 1054-1062 (PP)
- Tzounis et al., AIP Conference Proceedings 1646, (2015) 138 (PC)
- Tzounis et al., Polymer, 55 (2014) 21, 5381-5388 (PC)
- Liebscher et al., Composites Science and Technology 101(2014), 133-138 (PC)

Publications of IPF on TE materials with reduced Graphene Oxide

- Gnanaseelan et al., Materials Chemistry and Physics 2019, 229, 319-329 (SBS/rGO)

Publications of IPF on TE materials with carbon nanofibres

- Paleo et al., Polymers, 2022, 14, 4803 (PEEK)
- Paleo et al., ACS Applied Engineering Materials, 2023, 1(1), 122-131 (textile)
- Paleo et al., Polymers, 2022, 14(2), 269 (PP)
- Paleo et al., Polymer Journal 2021, 53, 1145–1152 (PP)

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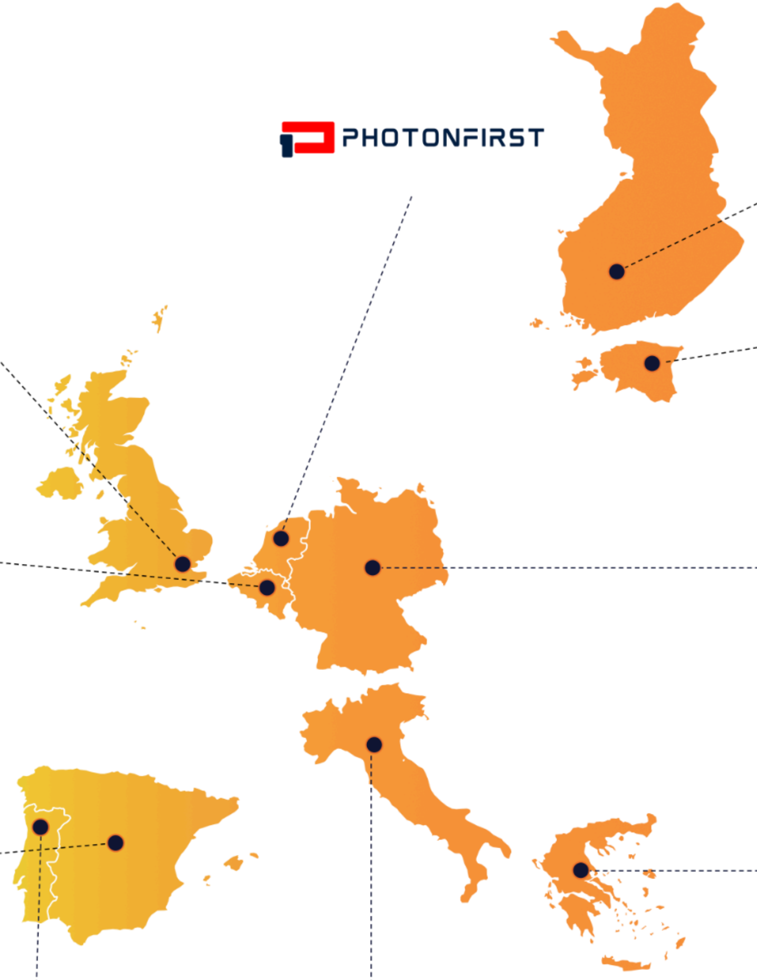

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Thank you

Department Functional Nanocomposites and Blends
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