Polymer-SWCNT composites for recovering waste heat into electrical energy

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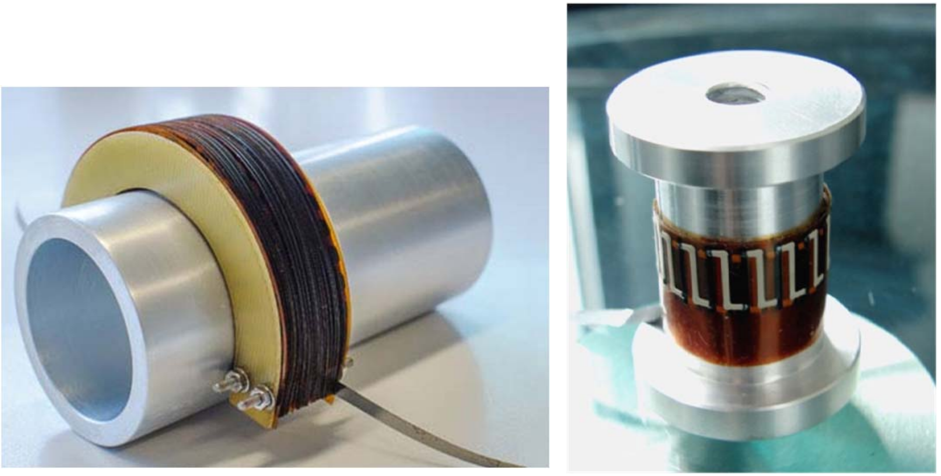
Outline

- o Basics of thermoelectric: The Seebeck effect
- o Advantages of polymers
- o Results on melt mixed polymer composites:

  Polypropylene (PP) with **singlewalled carbon nanotubes (SWCNTs)→ p- and n-type materials**
- o Summary, Outlook & Conclusions

The fiction:

Waste heat (even small amounts) used to generate electrical energy
Thermoelectric makes sensors working energy autonomous
Polymer based materials do the job



Prototype thermoelectric generator uses waste heat at the surface of pipes

Source: Fraunhofer IWS, Germany

Example paper machine: heat generated by drying processes enables the use of sensors controling the production process

Source: Fraunhofer IZM, Germany

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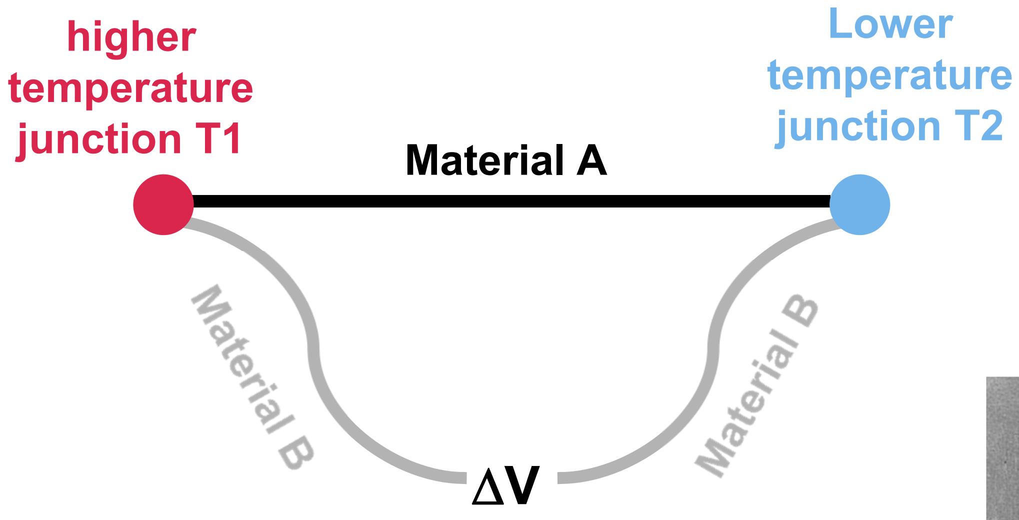
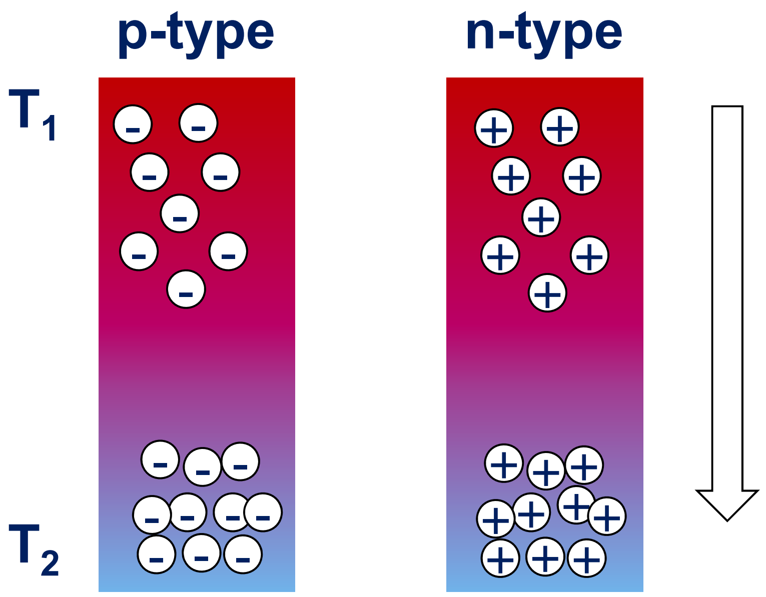
Thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa



When the two junctions are kept at different temperatures, a thermovoltage is produced in the circuit.

Discovered by Thomas Johann Seebeck in 1821

Seebeck/thermoelectric effect



dominant with holes

dominant with electrons

temperature gradient

⇩

charge carrier diffusion

⇩⇧

electrical voltage ΔV

$$S = -(U_1 - U_2) / (T_1 - T_2)$$

S: Seebeck coefficient, µV/K

S is a material constant

p-type: $S > 0$

n-type: $S < 0$

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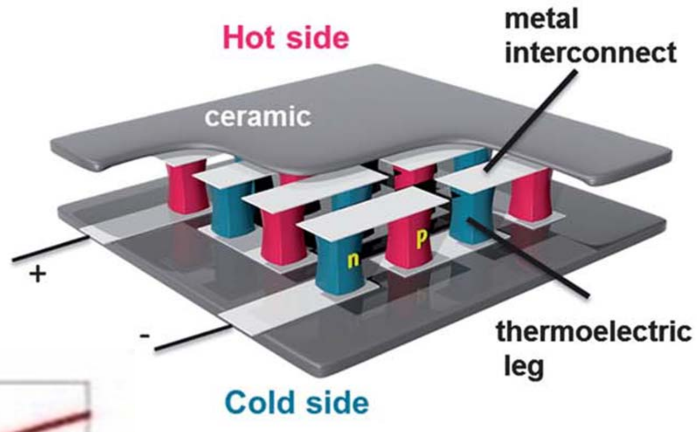
Material Evaluation:

Figure of merit: $ZT = (\sigma S^2/\kappa) * T$

σ: electrical conductivity [S/m]
S: Seebeck coefficient [V/K]
T: absolute temperature [K]
κ: thermal conductivity [W/mK]
σS^2: power factor PF [W/(mK²)]

Thermoelectric Generator (TEG)



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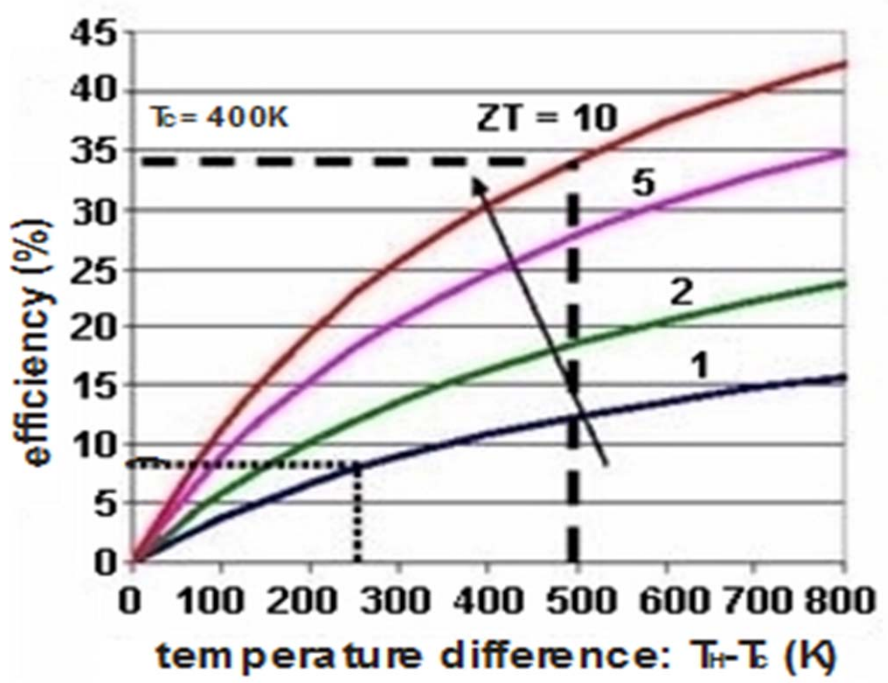


[2]

1: O. Bubnova, X. Crispin. Towards polymer-based organic thermoelectric generators, Energy Environ. Sci., 2012, 5, 9345
2: https://www.tu-chemnitz.de/physik/OFGF/research/thermoelectrics.php

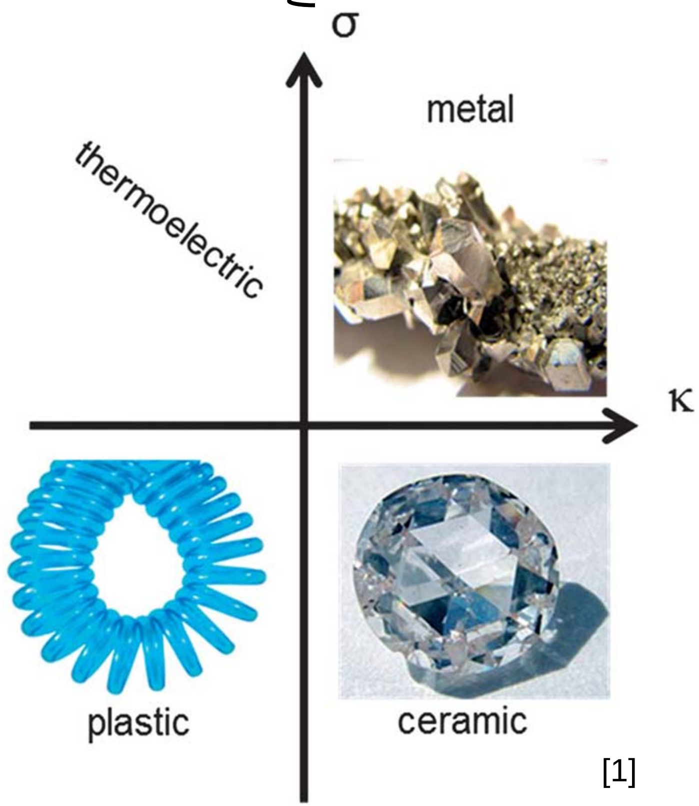
State of the art- TE materials

σ:	electrical conductivity	[S/m]
S:	Seebeck coefficient	[V/K]
T:	absolute temperature	[K]
κ:	thermal conductivity	[W/mK]
σS^2:	power factor	[W/(mK^2)]

Requirements as TE materials

Figure of merit: $ZT = (\sigma S^2/\kappa) * T$

high ZT
- **high power factor (σS^2)** ⇨ heat conversion to electricity
- **low κ** ⇨ large temperature gradient



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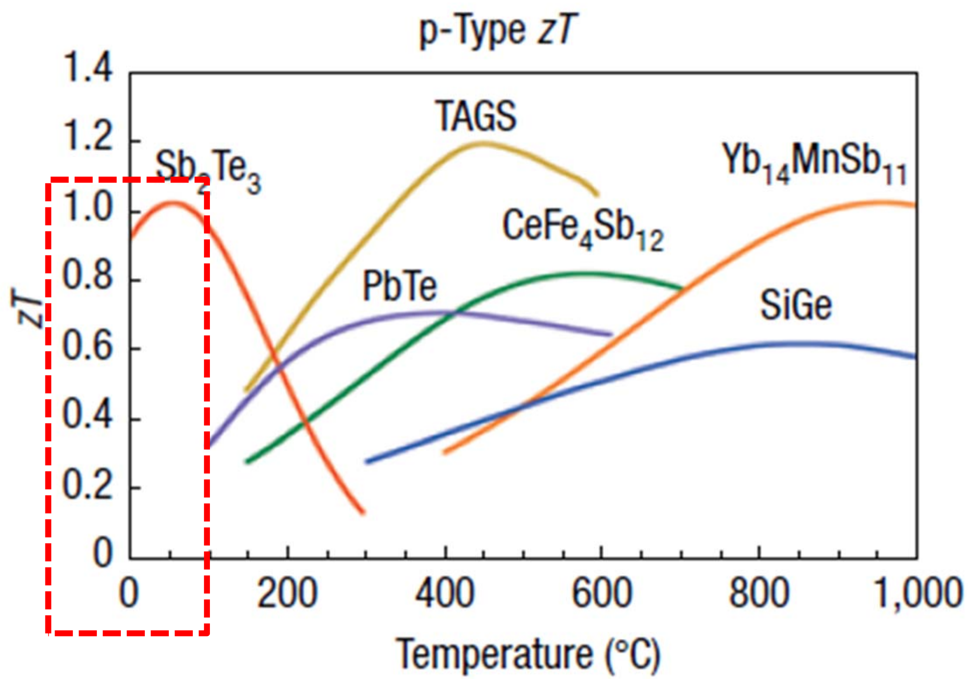


ZT of state of the art commercial materials [2]
(semiconductors, oxide, Half-Heusler-compounds, clathrates, silizides, antimonides, tellurides)

1: O. Bubnova, X. Crispin. Towards polymer-based organic thermoelectric generators, Energy Environ. Sci., 2012, 5, 9345
2: G. J. Snyder, E. S. Toberer, Complex thermoelectric materials, Nat. Mat., 2008, 7, 105-114

Why (thermoplastic) polymers?

Advantages of polymers for low T applications (<150°C)

- Available and low cost
- Lightweight, comparably environmental friendly
- Flexible and adaptable (different shapes)
- Easily manufactorable with existing processing methods
- Low thermal conductivity (0.1-0.5 W/mK)

Polymer based thermoelectric (TE) materials

Intrinsically electrical conductive (C) polymers (ICP)
polyaniline, P3HT, PEDOT:PSS, 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, solution or melt processable with e.g. CB, CNT, (graphene), …

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

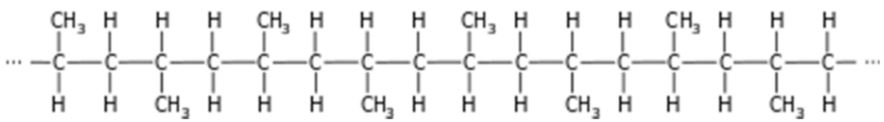
Melt processable thermoplastic matrices: scalable to mass production, easy to be shaped

Motivation

How powerful are melt mixed composites of insulating common polymers filled with carbon nanofillers for TE applications?

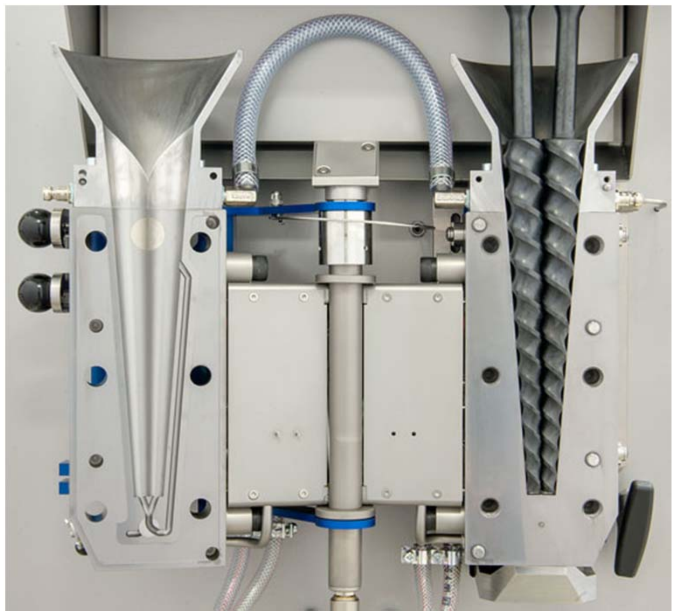
What are influencing factors on
- Conductivity
- Seebeck coefficient
- Power factor
- (Figure of Merit)

- Polypropylene (PP) with SWCNTs



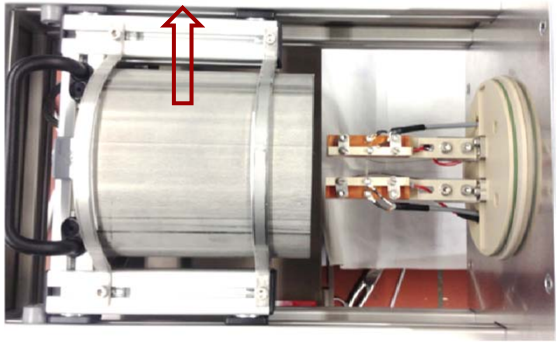
- Small scale melt mixing
- Prototype modules

Xplore microcompounder 15 ccm

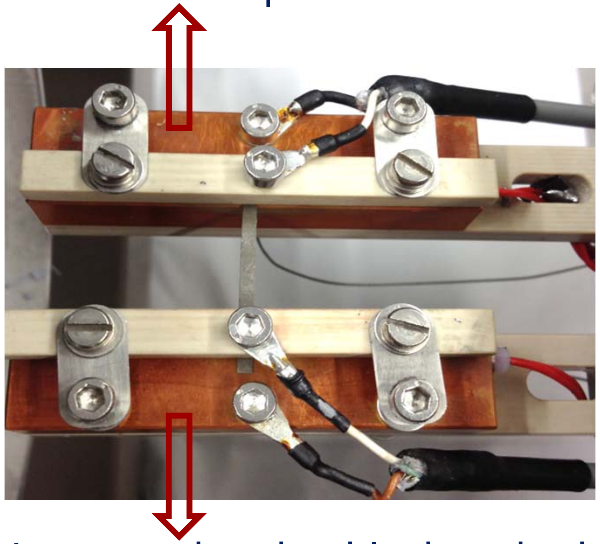


Development of a new measuring device (in-house built)

heating chamber to control the environmental temperature

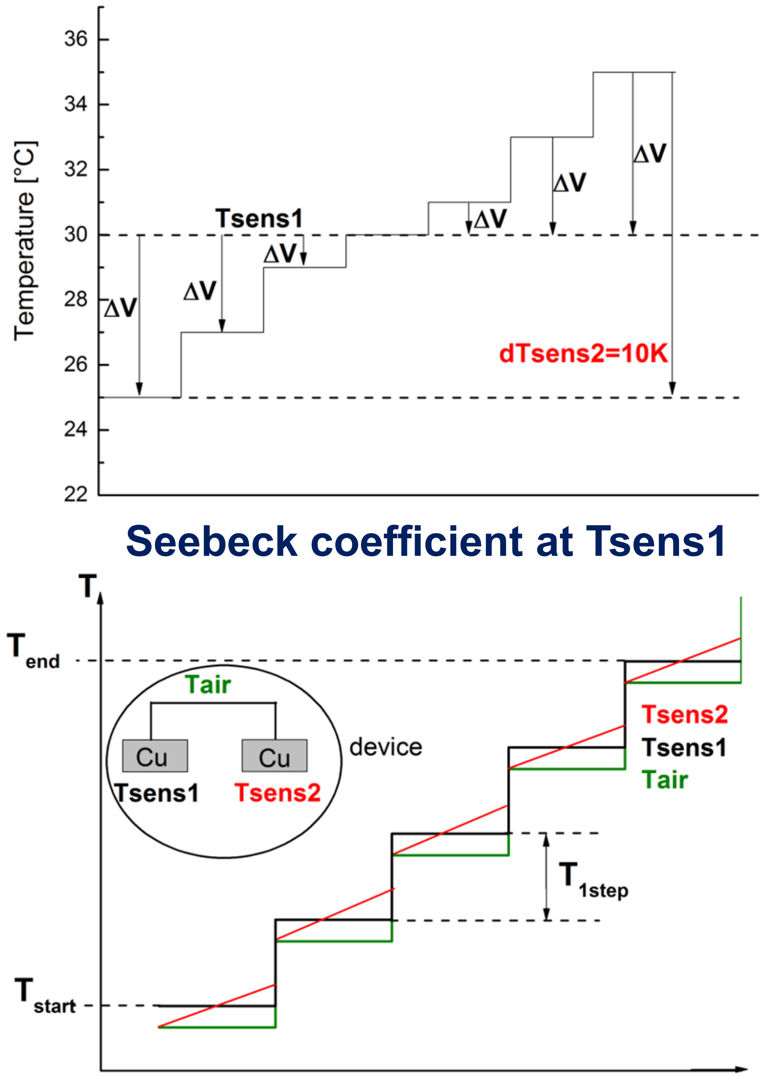


Stage 2: copper heating block embedded with heater and temperature control



copper as reference material

Stage 1: copper heating block embedded with heater and temperature control



Seebeck coefficient at Tsens1

Tsens1: from 30°C to 110°C

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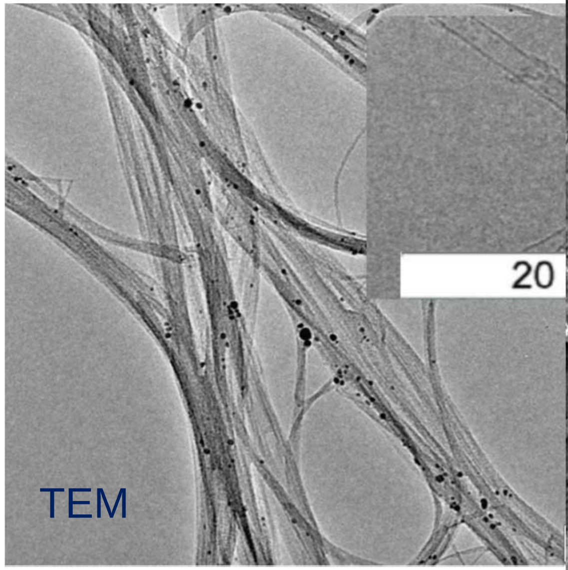
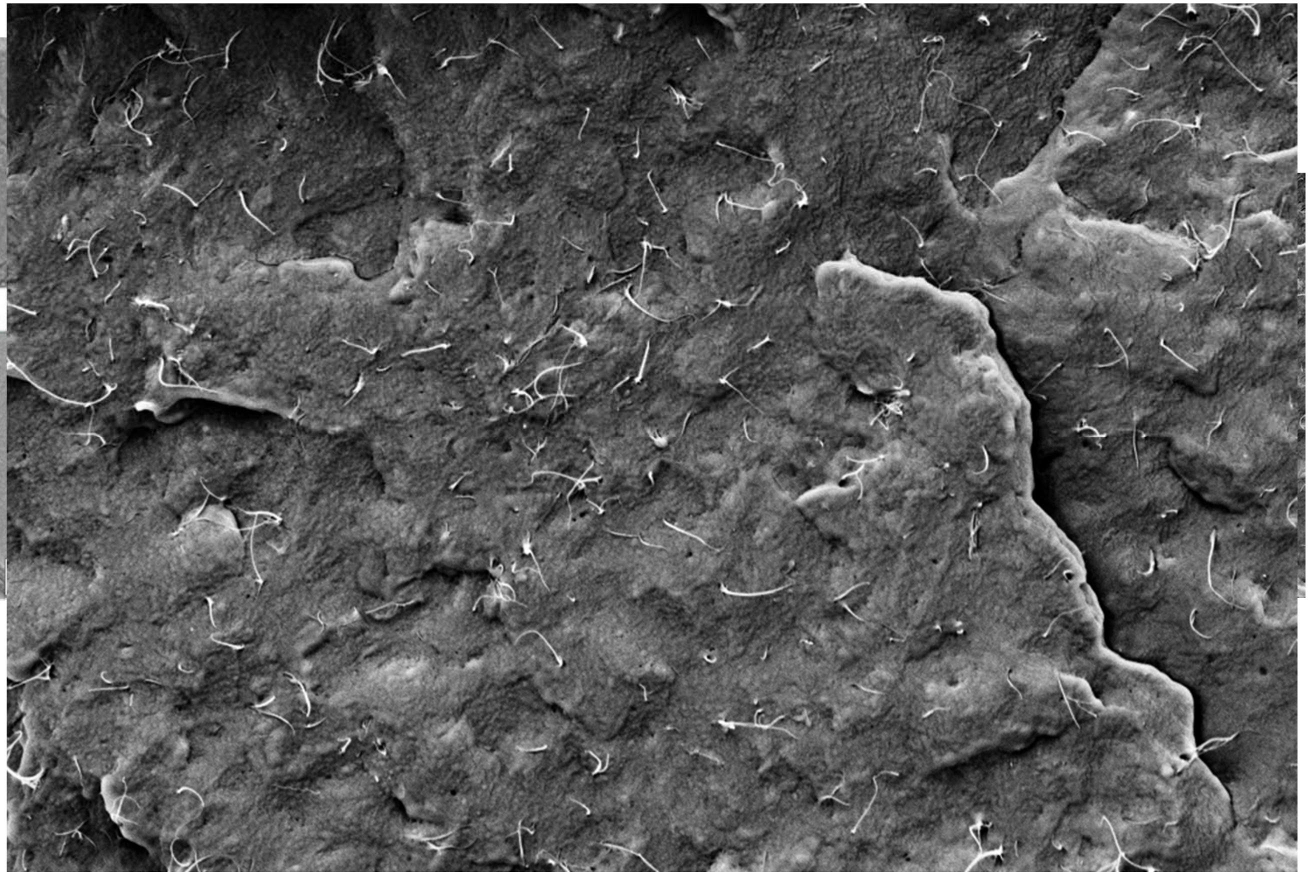
Melt processed polymer composites – Influence of SWCNT modification & content

SWCNT named TUBALL ™ from company OCSiAl Ltd.

- shown to be very long, straight and pure
- even if bundles are still existent electrical performance in composites very good
- Electrical percolation in PP below 0.1 wt%





From Raman:
Diameter 1.0 - 2.2 nm
maximum at 1.6 nm SWCNT

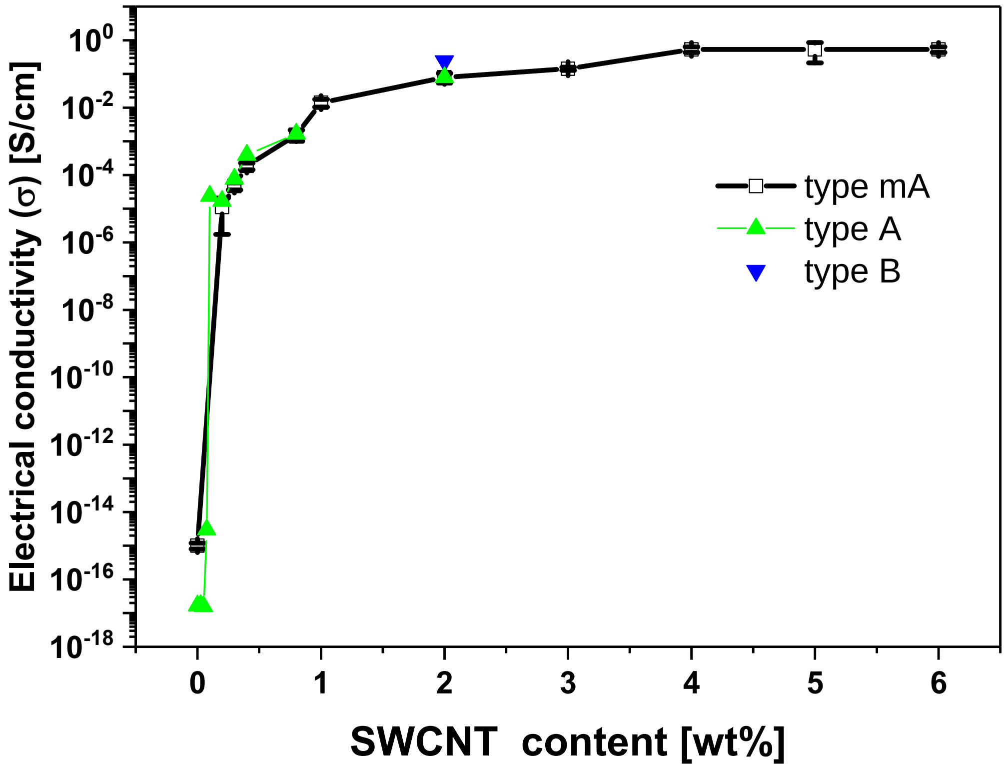
Length up to 5 μm
>75 wt% purity

B. Krause, P. Pötschke, E. Ilin and M. Predtechenskiy, Melt mixed SWCNT-polypropylene composites with very low electrical percolation, Polymer 98 (2016), 45-50, doi: 10.1016/j.polymer.2016.06.004

Melt processed polymer composites – Influence of SWCNT modification
Selection of 3 different (research) types:

- o singlewalled CNTs (type A and B, both unmodified but different synthesis conditions)
- o oxidized singlewalled CNTs (mA, type A was plasma modified resulting in oxygen groups)

- Polypropylene **Moplen HP 400R**, LyondellBasell Industries
- Percolation sets with types SWCNT A and mA, composites 2 wt% of all SWCNT materials
- Melt-mixing using DSM Xplore 15 ccm @ 210°C, 250 rpm, 5 min



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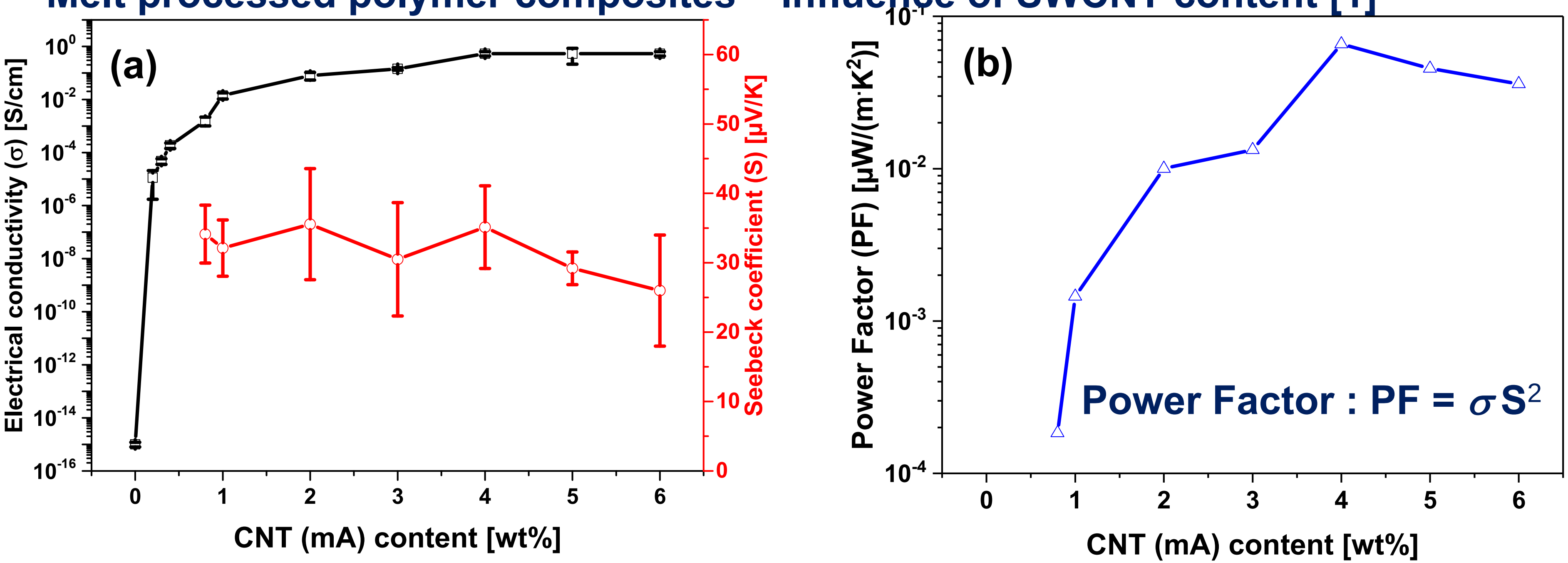
Melt processed polymer composites – Influence of SWCNT content [1]



TEM image of plasma oxidized singlewalled CNTs (type mA)

- Higher Seebeck coefficient than in melt mixed composites with multiwalled CNTs (35.6 vs. 11.5 µV/K)*
- Optimized power factor by adjusting the CNT concentration (4 wt%)
- * M. Liebscher, T. Gärtner, L. Tzounis, M. Micusik, P. Pötschke, M. Stamm, G. Heinrich, B. Voit, Influence of the MWCNT surface functionalization on the thermoelectric properties of melt mixed polycarbonate, Composites Science and Technology, 2014, 101, 133-138

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]1] J. Luo, B. Krause, and P. Pötschke, Melt-mixed thermoplastic composites containing carbon nanotubes for thermoelectric applications, AIMS Materials Science, 3(2016) 3, 1054-1062

Results: Materials based on PP and SWCNTs

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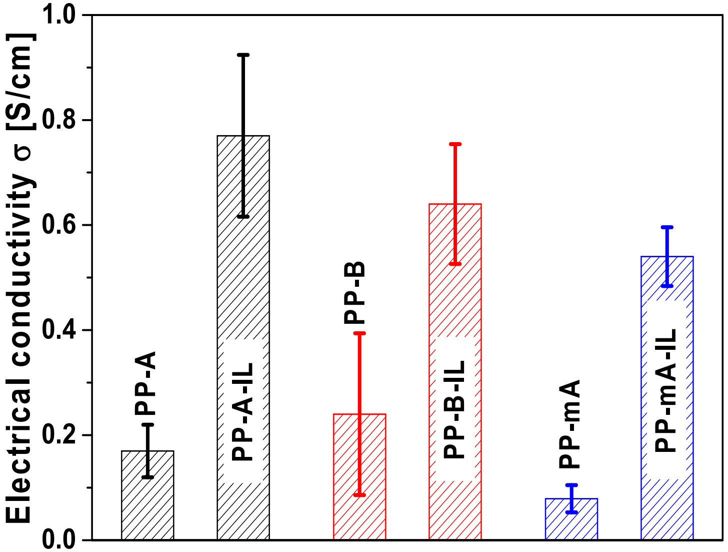
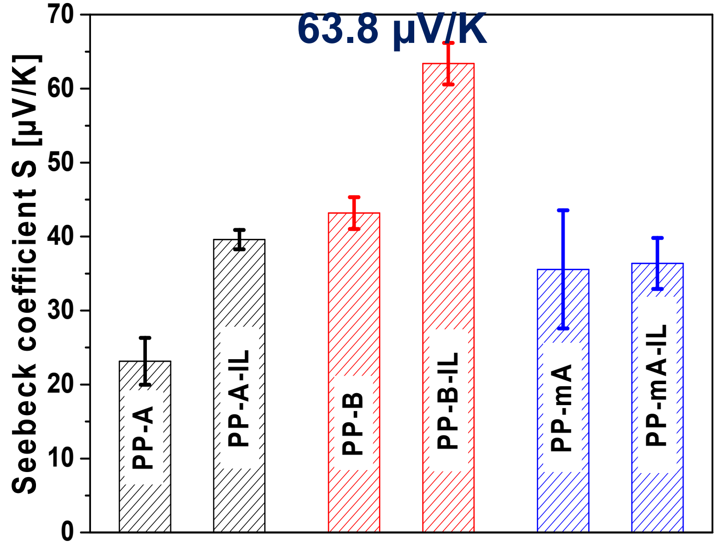
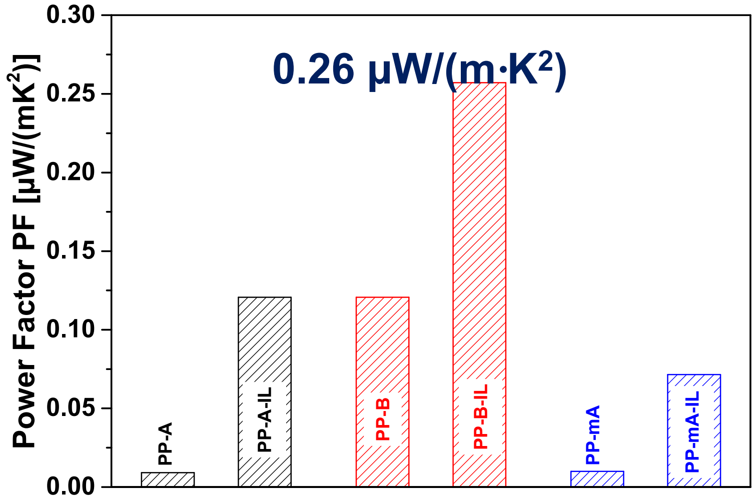
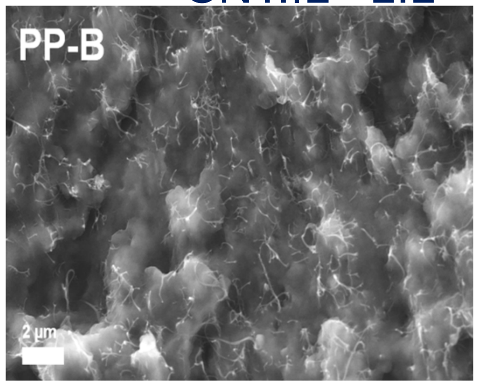
Melt processed polymer composites – Influence of addition of Ionic Liquid (IL) [2]







2.0 wt% SWCNTs
CNT:IL =1:1

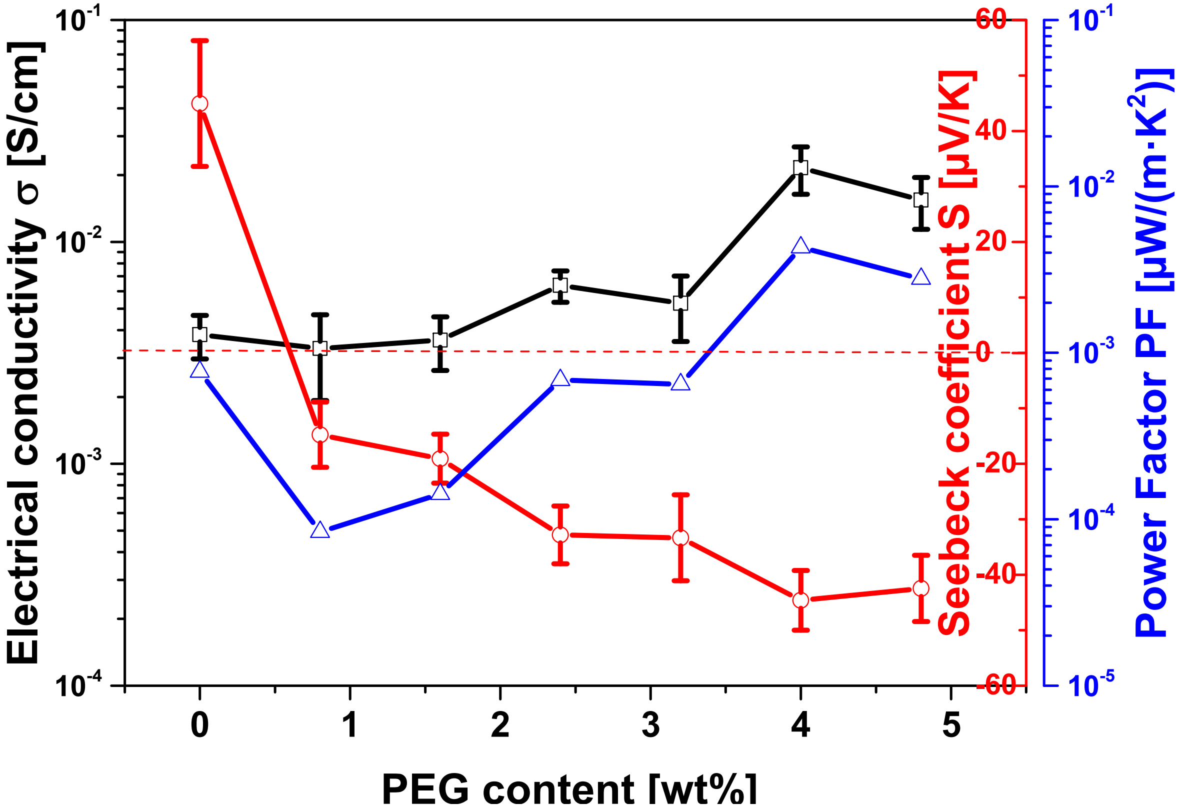


- Addition of IL during mixing improves the electrical conductivity of composites filled with all three types of SWCNTs, highest S and PF for SWCNT type B after IL addition

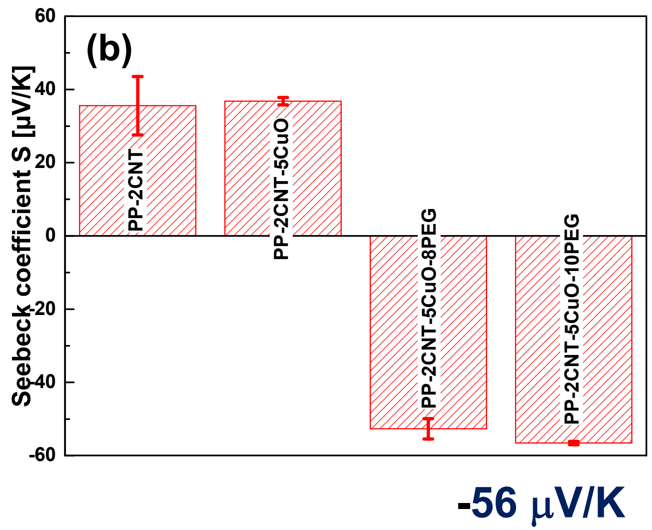
[2] J. Luo, P. Pötschke, and B.Krause, Polymer Carbon Nanotube Composites for Thermoelectric Applications, Polymer Carbon Nanotube Composites for Thermoelectric Applications, lecture S02-34, Proceedings of the 32nd International Conference of the PPS, July 25-29, 2016 Lyon, France

Melt processed polymer composites – Switching from p-type to n-type [3]

0.8 wt% SWCNT, 5 wt% CuO



2 wt% SWCNT, 5 wt% CuO



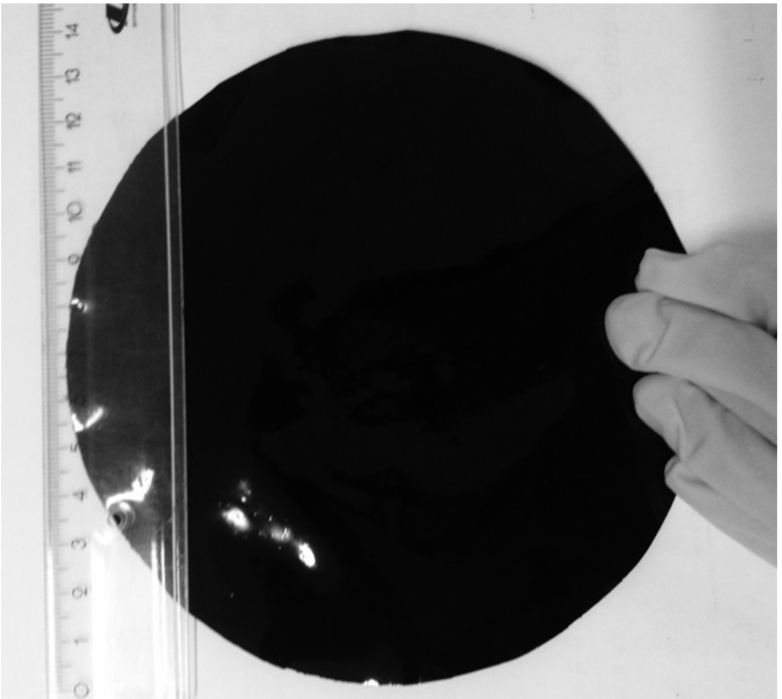
- Addition of polyethylene glycol (PEG, M_n= 10.000 g/mol) during mixing improves the electrical conductivity of composites and switches behavior from p-type to n-type already at 0.8 wt% addition (SWCNT:PEG=1:1)
- Doping of CNTs by the additive

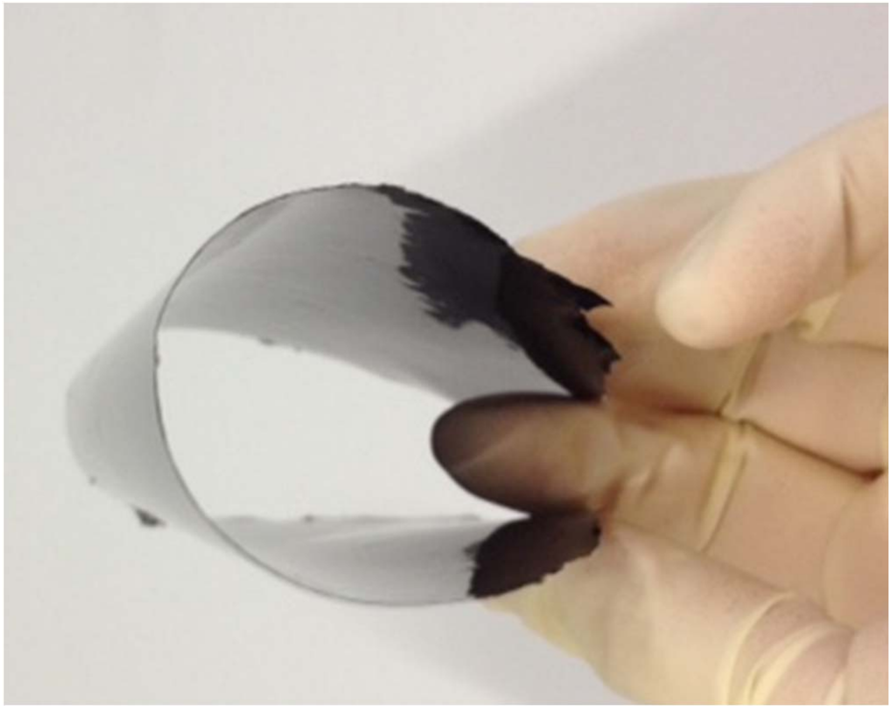
[3] J. Luo, G. Cerretti, B. Krause, L. Zhang, T. Otto, W. Jenschke, M. Ullrich, W. Tremel, B. Voit, P. Pötschke, Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol, Polymer,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

Prototypes: melt mixed composites

Prototype modules for TEG thermoelectric generators

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:
Planary 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)

[3] 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

Prototypes: melt mixed composites

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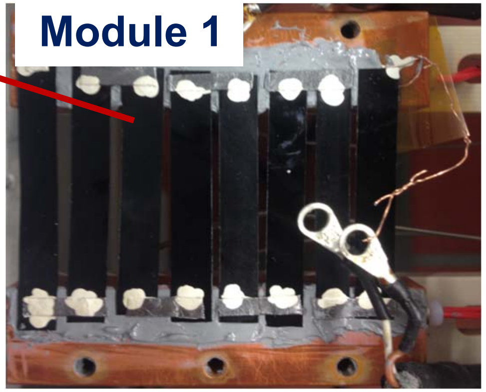
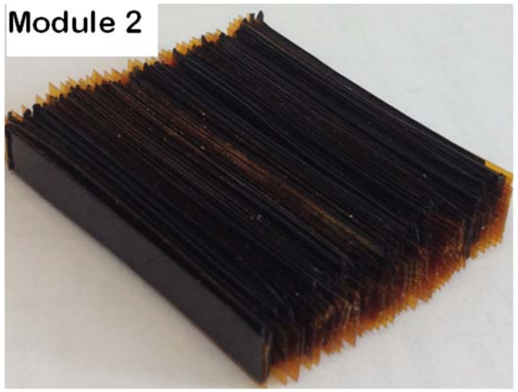
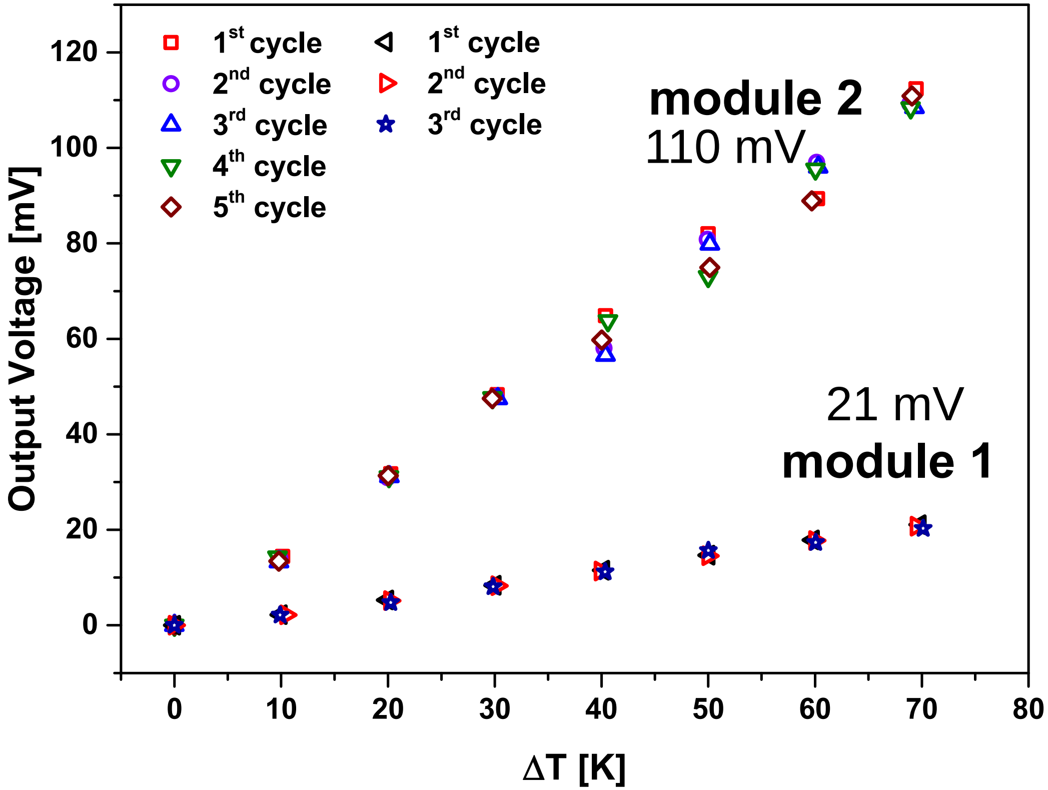
For module 1:
4 thermocouples connections were made by silver paste and graphite foil



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

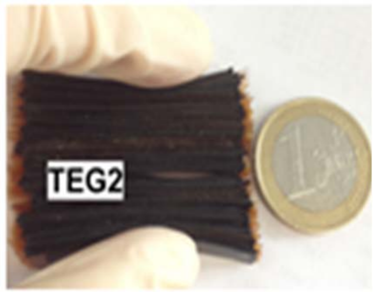
accordion like structure





PP +2 wt% SWCNT p-type
PP+ 2wt% SWCNT+additive n-type

Planary type: TEG1 with 4 thermocouples (4 layers p-type & 4 layers n-type)
Vertical type (accordion like): TEG2 with 49 thermocouples (49 layers of p-type and 49 layers of n-type)



[3] 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

Summary and Outlook

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Polymer based TE materials still have much **lower efficiency values than traditional TE materials** (max. ZT in our research $1.6 * 10^{-4}$ 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
- Plasma oxidation of SWCNT and addition of IL enhances S and PF
- **Best values of our research: S 63.8 µV/K, PF 0.26 µW/mK²**
- **Switching from p-type to n-type** easily possible
- Based on these melt mixed composites two modules were successfully fabricated to demonstrate the possibility of using melt mixing to fabricate thermoelectric materials and thereby thermoelectric generators (**max. 110 mV so far**)

New ideas: combined filler systems like CuO and TiO2 with SWCNTs, blend structures

Thanks

- Support in sample preparation and morphology characterization by Mrs. Jentzsch-Hutschenreuther and Manuela Heber
- Support in setting up the instruments to Dr. Wolfgang Jenschke and Mathias Ullrich

Department Functional Nanocomposites and Blends 1.8.16

Thank you for your attention!