Electrically Conductive Biocomposites Based on PHBV and Wood-Derived Carbon Fillers

Christoph Unterweger[1], Matija Ranzinger[2], Jiri Duchoslav[3], Francesco Piana[4], Igor Pasti[5], Franz Zeppetzauer[1], Stefan Breitenbach[1], David Stifter[3], Christian Fürst[1], Matthias Mihalic[1]

[1] Wood K plus - Kompetenzzentrum Holz GmbH, Linz, Austria / [2] FTPO - Faculty of Polymer Technology, Slovenj Gradec, Slovenia
[3] Johannes Kepler University Linz, Center for Surface and Nanoanalytics (ZONA), Linz, Austria
[4] Czech Academy of Sciences - Institute of Macromolecular Chemistry, Prague, Czech Republic / [5] University of Belgrade – Faculty of Physical Chemistry, Belgrade, Serbia

International Conference on Composite Materials 2023, 30 July – 04 August 2023, Belfast

Wood K plus in Austria

R&D Institute for
Wood Composites &
Wood Chemistry

Founded in 2001

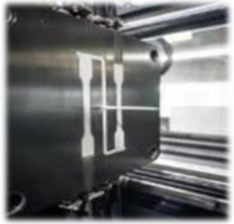
130 scientific employees

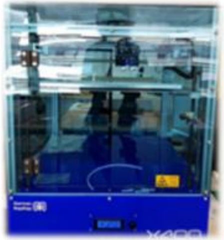
3 business units
1 cross sectional area
Sustainable Innovation and Impact Analysis

Leading Research Institute in the area wood and wood-related renewable resources

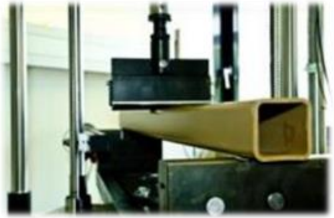
Biorefinery Processes and Composite Materials









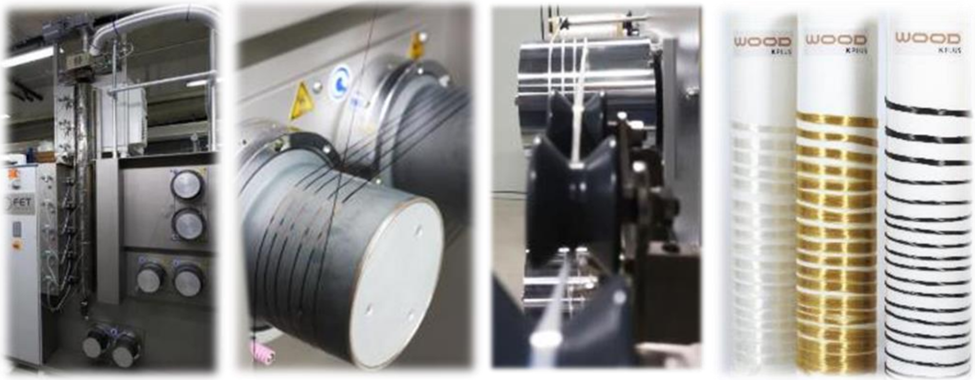




- Digesting Processes
  - Feedstocks and Products
- Biotechnological Process
  - Technology
- Chemical Process
  - Technology
- Biobased Fibers and
  - Carbon Materials
- Biobased Composites,
  - Applications and Processes

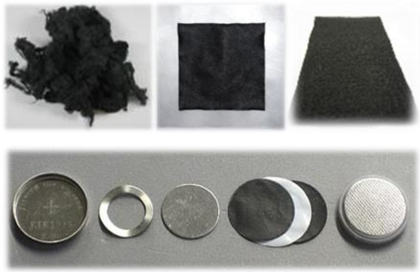
Biobased Fibers & Carbon Materials

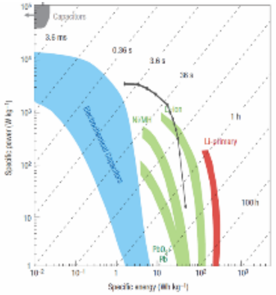
HT equipment

Bio-based continuous carbon fibers



Bio-based functional carbons / CF





Bio-based SiC ceramics

Background

Conventional polymers and carbons are fossil-based

- environmental concerns
- volatile price
- limited long-term availability

Increased use of biopolymers mostly PLA (compostable) or PHAs (biodegradable)

→ Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) very promising

+ biodegradable, available at industrial scale, good mechanical properties

- slow crystallization, susceptible to thermal degradation

PHBV/carbon composites show interesting properties for electrical applications

In PHBV/carbon composites mostly fossil-based carbons like CNT, graphene or carbon black are used

→ "Biocomposites" should contain biopolymers <u>and</u> bio-based fillers

WOOD K plus is working on PHBV synthesis, bio-based carbons, composites and processing

Approach

Materials

- PHBV type ENMAT™ Y1000P (TianAn Biologic Material Co. Ltd., Ningbo, CHN)
- cellulose fibers, type lyocell, 300 µm, 1.3 dtex (Lenzing AG, Lenzing, AUT)
- wood dust Arbocel® C100 (J. Rettenmaier & Söhne GmbH + Co KG, Rosenberg, GER)

Methods

- carbonization at various temperatures: 900, 1500, 2000 and 2300 °C
- carbon filler characterization: geometry, EDX, XPS, XRD, pH, porosity
- compounding (internal mixer, 173 °C, constant volume, 0 – 20 vol% fillers)
- injection molding (dog-bone test specimen, nozzle 190 °C, mold 60 °C)
- composite characterization (MFI, GPC, filler dimensions, tensile, flexural, impact testing, conductivity)

For more details, see:

Unterweger C et al. Electrically Conductive Biocomposites Based on Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and Wood-Derived Carbon Fillers. Journal of Composites Science. 2022; 6(8):228. https://doi.org/10.3390/jcs6080228

Sample Overview

sample	filler type	$T_{carb.}$ [°C]	filler content [vol.%]
PHBV	-	-	0
PHBV_CF900_10	carb. cellulose	900	10
PHBV_CF1500_10	carb. cellulose	1500	10
PHBV_CF2000_10	carb. cellulose	2000	10
PHBV_CF2300_10	carb. cellulose	2300	10
PHBV_CF2000_5	carb. cellulose	2000	5
PHBV_CF2000_15	carb. cellulose	2000	15
PHBV_CF2000_20	carb. cellulose	2000	20
PHBV_CW900_10	carb. wood	900	10
PHBV_CW1500_10	carb. wood	1500	10
PHBV_CW2000_10	carb. wood	2000	10
PHBV_CW2300_10	carb. wood	2300	10
PHBV_CW2000_5	carb. wood	2000	5
PHBV_CW2000_15	carb. wood	2000	15
PHBV190 *	-	-	*0*
PP_CF2000_5 **	*carb. cellulose*	*2000*	*5*
PP_CF2000_10 **	*carb. cellulose*	*2000*	*10*
PP_CF2000_15 **	*carb. cellulose*	*2000*	*15*

*** MFI & GPC only***
**** conductivity only***

Repeated multiple times
- Very low viscosity
- Smallest T increase in mixer
- MFI too high
- Injection molding impossible

Goals
- Achievable property profiles
- Impact of filler geometry
- Impact of filler content
- Impact of carbonization T

Carbon Filler Analysis

sample	Length [µm]	L/D [-]	d_{002} [nm]	S_{BET} [m²/g]	Moisture [g/g %]	pH [-]	C_{EDX} [at.%]	O_{EDX} [at.%]	Na_{EDX} [at.%]	Ca_{EDX} [at.%]	C_{XPS} [at.%]	O_{XPS} [at.%]	Na_{XPS} [at.%]
CF900	259	32.8	0.375	174.0	1.09	10.8	95.69	3.95	0.25	0.00	84.5	9.6	5.9
CF1500	257	32.5	0.370	2.2	0.24	11.0	97.18	2.60	0.13	0.00	76.1	12.8	11.1
CF2000	251	31.8	0.352	1.3	0.03	6.3	98.09	1.76	0.02	0.00	100.0	0.0	0.0
CF2300	241	30.4	0.344	1.8	0.02	6.0	98.60	1.30	0.02	0.00	-	-	-
CW900	65	1.6	0.371	309.3	1.26	12.0	93.86	5.76	0.00	0.30	-	-	-
CW1500	68	1.6	0.359	4.7	0.19	10.3	95.98	3.68	0.00	0.20	98.9	1.1	0.0
CW2000	64	1.5	0.343	3.5	0.15	6.6	97.48	1.93	0.00	0.35	-	-	-
CW2300	69	1.5	0.342	3.7	0.09	6.8	97.71	2.13	0.00	0.03	-	-	-

Cellulose precursor contains small amounts of Na compounds which seem to accumulate at the fiber surface during carbonization at 1500 °C

→ These Na/O compounds seem to induce PHBV degradation → mechanism unclear

Overview: Properties

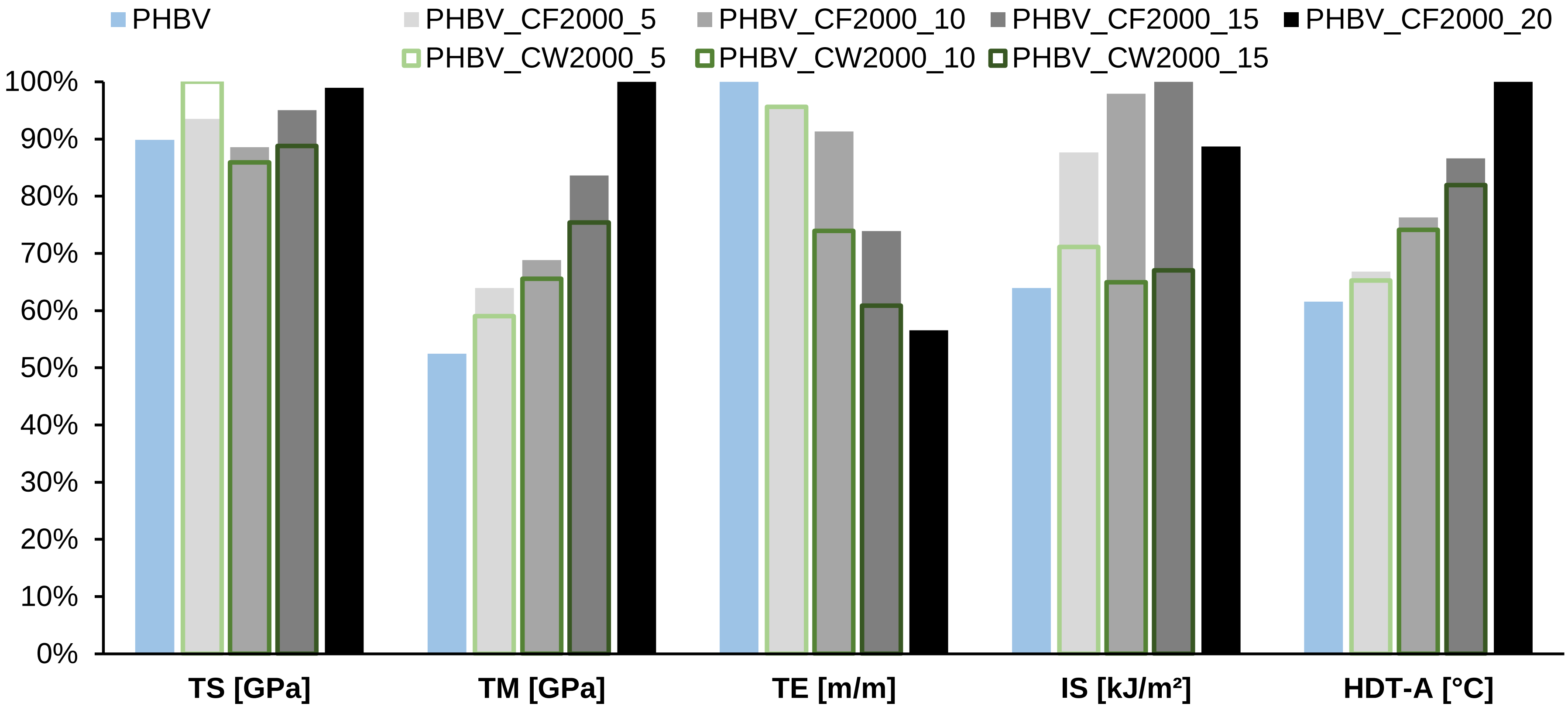
Sample	TS [MPa]	TM [GPa]	TE [m/m %]	IS [kJ/m²]	NIS [kJ/m²]	HDT-A [°C]	ρ [g/cm³]	σ [S/cm]
PHBV	34.5 ± 0.7	3.2 ± 0.1	2.3 ± 0.2	6.2 ± 0.2	1.3 ± 0.1	78.5 ± 4.6	1.246 ± 0.006	2.0E-12
PHBV_CF900_10	36.1 ± 0.1	4.1 ± 0.1	2.0 ± 0.2	9.9 ± 0.8	1.6 ± 0.2	100.2 ± 4.9	1.265 ± 0.008	8.0E-11
PHBV_CF1500_10	23.3 ± 3.8	5.1 ± 0.1	0.5 ± 0.1	3.6 ± 0.5	0.9 ± 0.1	107.6 ± 3.6	1.264 ± 0.005	3.0E-10
PHBV_CF2000_10	34.0 ± 0.1	4.2 ± 0.1	2.1 ± 0.1	9.5 ± 0.7	1.5 ± 0.1	97.3 ± 7.8	1.264 ± 0.001	8.3E-11
PHBV_CF2300_10	35.5 ± 0.1	4.5 ± 0.1	1.7 ± 0.1	11.5 ± 0.7	1.6 ± 0.2	96.8 ± 3.8	1.264 ± 0.001	1.0E-10
PHBV_CF2000_5	35.9 ± 0.1	3.9 ± 0.1	2.2 ± 0.1	8.5 ± 0.6	1.9 ± 0.3	85.2 ± 1.9	1.253 ± 0.003	4.0E-12
PHBV_CF2000_10	34.0 ± 0.1	4.2 ± 0.1	2.1 ± 0.1	9.5 ± 0.7	1.5 ± 0.1	97.3 ± 7.8	1.264 ± 0.001	8.3E-11
PHBV_CF2000_15	36.5 ± 0.2	5.1 ± 0.1	1.7 ± 0.1	9.7 ± 0.4	1.7 ± 0.3	110.4 ± 7.5	1.271 ± 0.002	6.2E-09
PHBV_CF2000_20	38.0 ± 0.2	6.1 ± 0.1	1.3 ± 0.2	8.6 ± 0.9	1.6 ± 0.5	127.5 ± 5.4	1.287 ± 0.002	6.9E-01
PHBV_CW900_10	34.7 ± 0.1	4.1 ± 0.1	1.6 ± 0.1	6.1 ± 0.1	1.4 ± 0.1	91.4 ± 4.2	1.265 ± 0.001	4.5E-12
PHBV_CW1500_10	34.0 ± 0.4	4.2 ± 0.1	1.6 ± 0.1	6.0 ± 0.3	1.4 ± 0.1	93.9 ± 4.4	1.264 ± 0.001	7.2E-12
PHBV_CW2000_10	33.0 ± 0.1	4.0 ± 0.1	1.7 ± 0.1	6.3 ± 0.2	1.6 ± 0.2	94.5 ± 3.6	1.265 ± 0.006	3.7E-12
PHBV_CW2300_10	32.7 ± 0.2	3.9 ± 0.1	1.7 ± 0.1	6.4 ± 0.3	1.9 ± 0.3	92.4 ± 3.8	1.269 ± 0.001	3.6E-12
PHBV_CW2000_5	38.4 ± 0.3	3.6 ± 0.1	2.2 ± 0.1	6.9 ± 0.4	1.6 ± 0.2	83.2 ± 2.4	1.255 ± 0.002	5.0E-12
PHBV_CW2000_10	33.0 ± 0.1	4.0 ± 0.1	1.7 ± 0.1	6.3 ± 0.2	1.6 ± 0.2	94.5 ± 3.6	1.265 ± 0.006	3.7E-12
PHBV_CW2000_15	34.1 ± 0.2	4.6 ± 0.1	1.4 ± 0.1	6.5 ± 0.4	1.6 ± 0.3	104.5 ± 4.2	1.273 ± 0.004	8.7E-12

Mw after compounding is 82 kDa → 207 kDa for virgin PHBV, average in all other compounds is 173 kDa

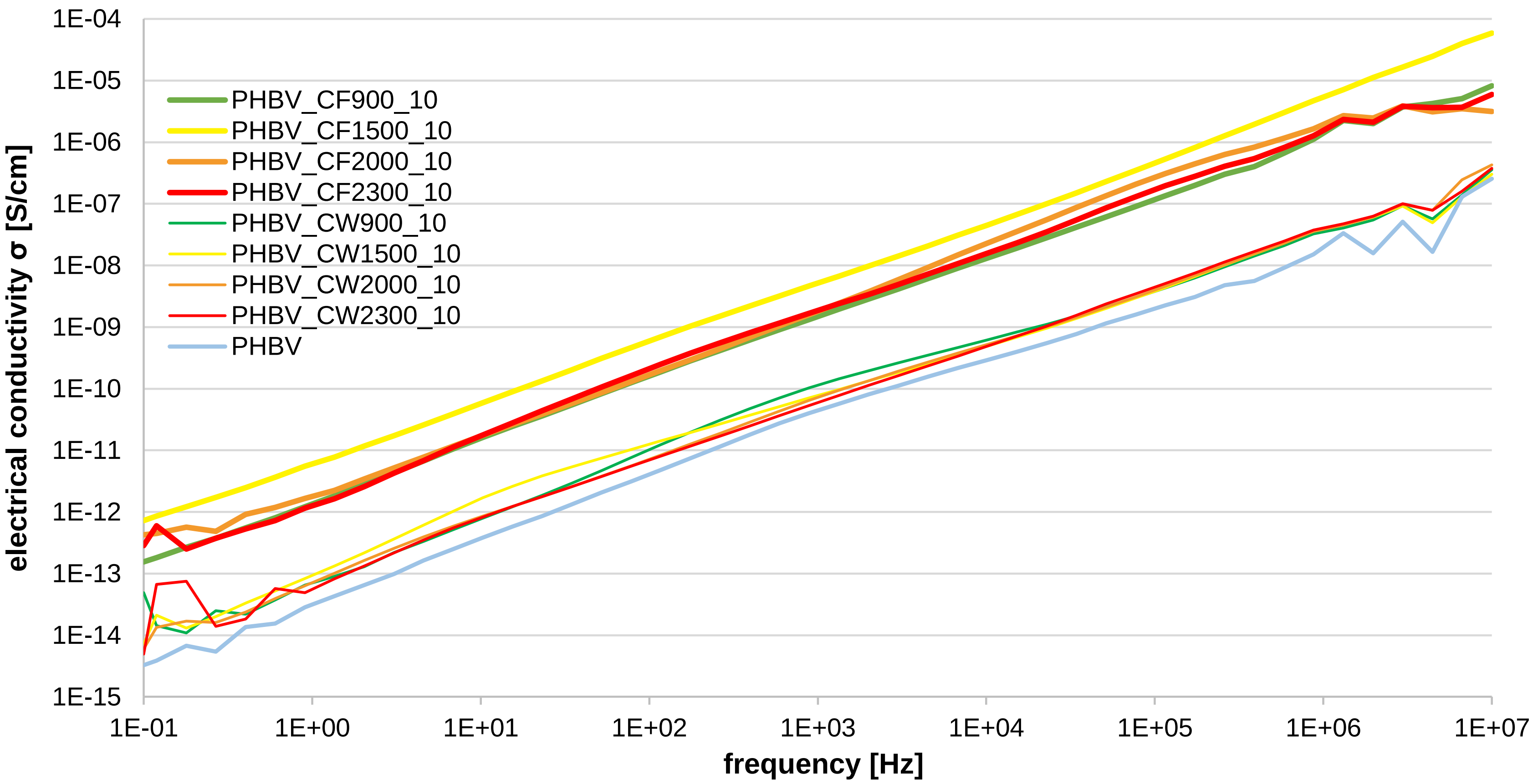
Mechanical properties: No significant impact of filler type, improved at higher filler content

Conductivity: Fibers superior to particles, massive impact of fiber content

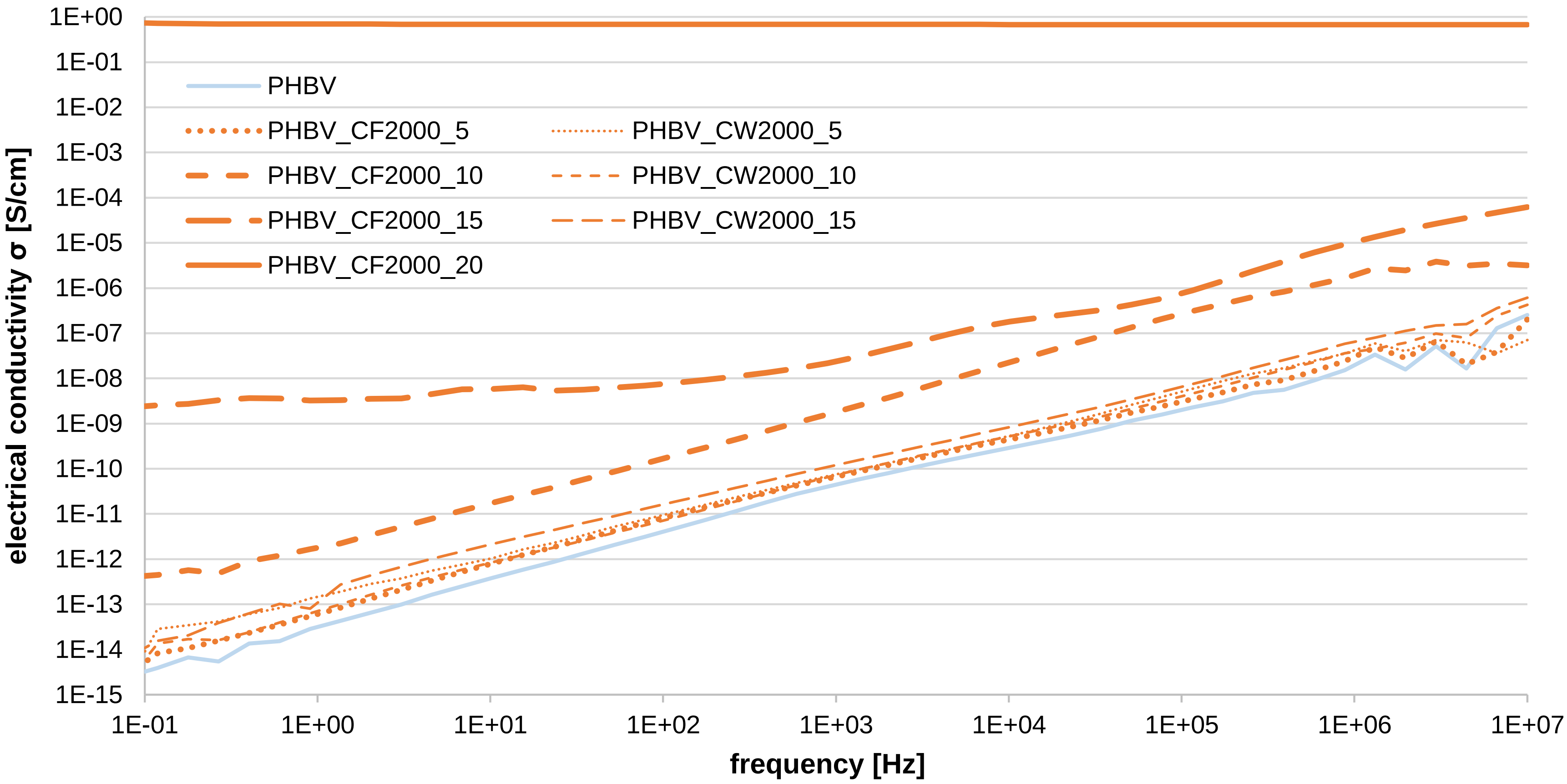
Mechanical Properties



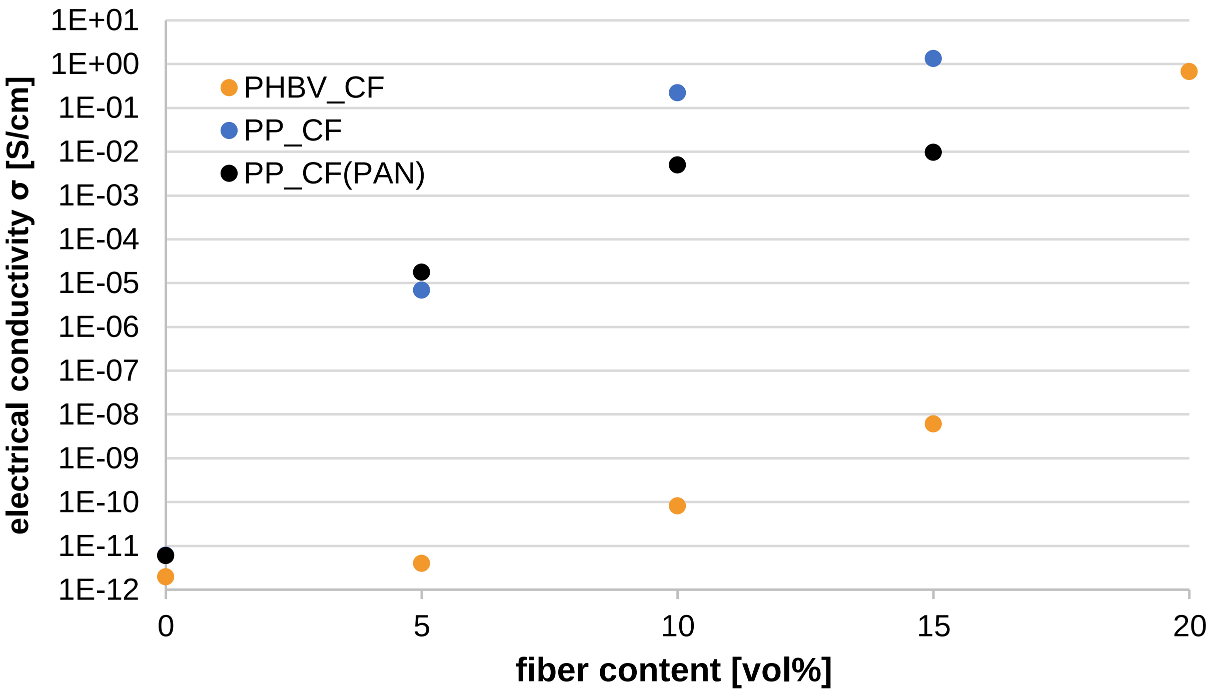
Electrical Conductivity



Electrical Conductivity



Electrical Conductivity (at 50 Hz)



PP is thermally more stable
Higher processing T possible
→ 230 °C (T_m + 65 °C)
→ lower viscosity / less shear
→ longer fibers
→ L/D = 19 (12 in PHBV)

Increased L/D leads to shift of percolation threshold to lower fiber content
Percolation threshold of PP/CF2000 similar PP with commercial CF
Higher conductivity values achievable in PP/CF2000 compared to PP/CF(PAN)

Summary and Outlook

- Different **bio-based carbon fillers** can be prepared
- **Accumulation of Na/O compounds at surface of CF1500** → degradation of PHBV during melt mixing
- **Property profiles of PHBV/carbon** have been evaluated. **Improved performance through:**
  - → **higher filler content**
  - → **increased L/D**
  - → **no significant impact of carbonization temperature on conductivity**
- **Higher achievable conductivities with carbonized cellulose** fibers compared to commercial CF
- Ongoing/open work:
  - → **Use of fibrous biomass/waste streams** for carbon filler preparation
  - → PHBV composites **using longer carbonized cellulose fibers**

Acknowledgment

i3Sense is a COMET Module within the COMET – Competence Centers for Excellent Technologies Programme and funded by BMK and BMAW. COMET is managed by FFG.

i3Sense
Intelligent
Integrated
Impregnated

Bundesministerium
Klimaschutz, Umwelt,
Energie, Mobilität,
Innovation und Technologie

Bundesministerium
Arbeit und Wirtschaft

FFG
Forschung wirkt.

Kompetenzzentrum Holz GmbH
(Wood K plus)

Altenberger Strasse 69
4040 Linz, Austria
Tel.: +43 (0)732 2468 6750
Fax: +43 (0)732 2468 6755
E-mail: zentrale@wood-kplus.at
Homepage: www.wood-kplus.at

Dr. Christoph Unterweger
Team Leader
Biobased Fibers and Carbon Materials
Altenberger Strasse 69
4040 Linz, Austria
Tel.: +43 (0)732 2468 6758
mobile: +43 (0)676 897 44 534
E-mail: c.unterweger@wood-kplus.at