TERAHERTZ COMPLEX CONDUCTIVITY OF NANOCELLULOSE-PEDOT:PSS COMPOSITE FILMS

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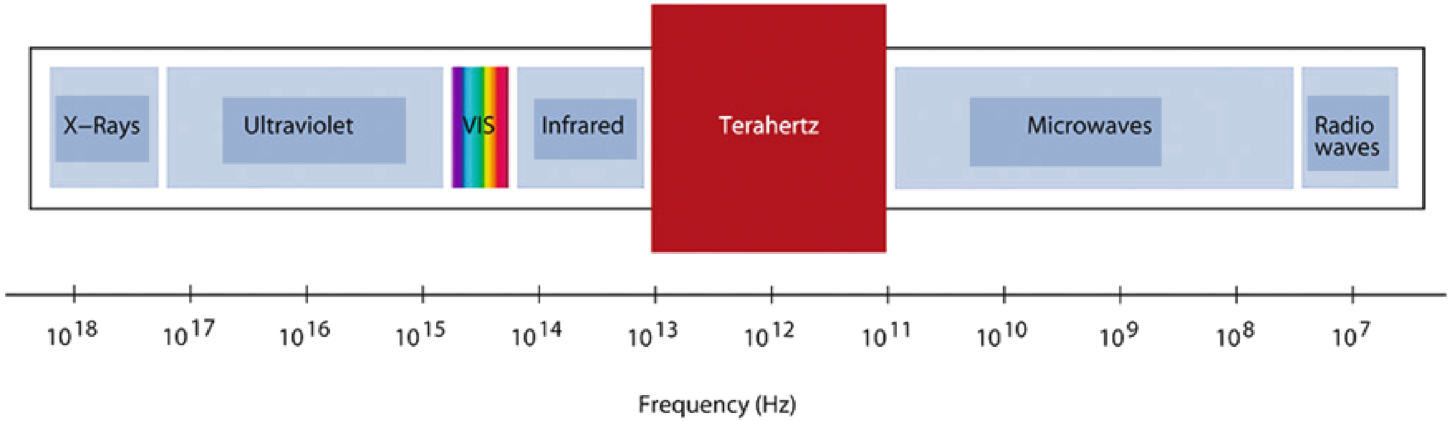
BACKGROUND: TERAHERTZ (THz) RADIATION

A frequency band between the far infrared and microwave region
Typical frequency range: 0.3 – 3.0 THz
Typical wavelength range: 1 000 µm – 100 µm



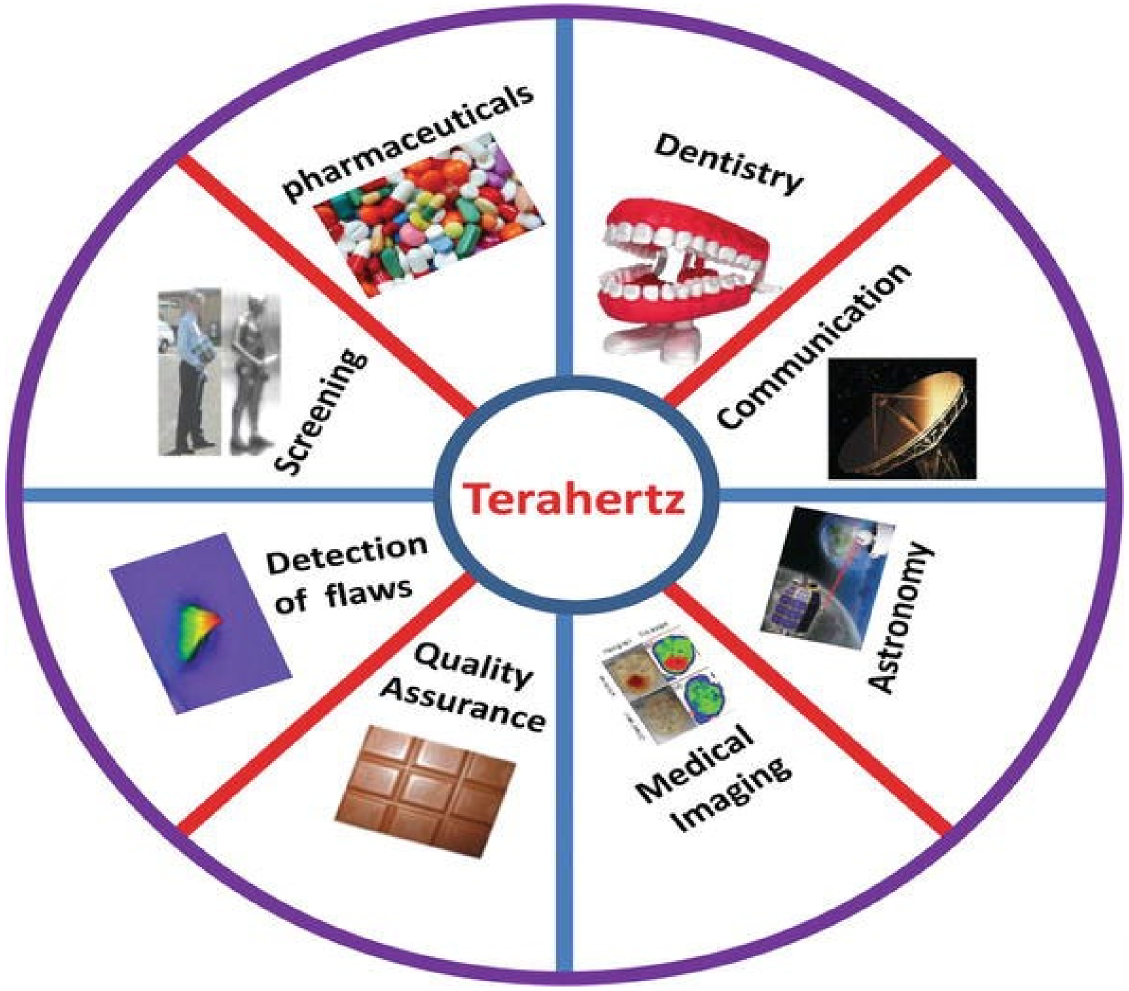
Photoconductive antennas were demonstrated for high-intensity THz waves with a good signal-to-noise ratio. [1]

THz time-domain spectroscopy (THz-TDS) was demonstrated for the molecular absorption lines of ambient water vapor in 0.5–1.5 THz [2] that was the milestone of molecular sensing with a fingerprint spectral feature in the THz region.

These finding opened up the wide-scale applications of THz radiation in various fields.

[1] M. van Exter *et al.* Appl. *Phys. Lett.* **55**, 337 (1989).
[2] M. van Exter *et al. Opt. Lett.* **14**, 1128 (1989).

THz APPLICATIONS



THz imaging technology can detect and confirm not only hidden explosives and weapons but also some CBREs (chemical, biological and radiological elements), solids, powders and liquids.

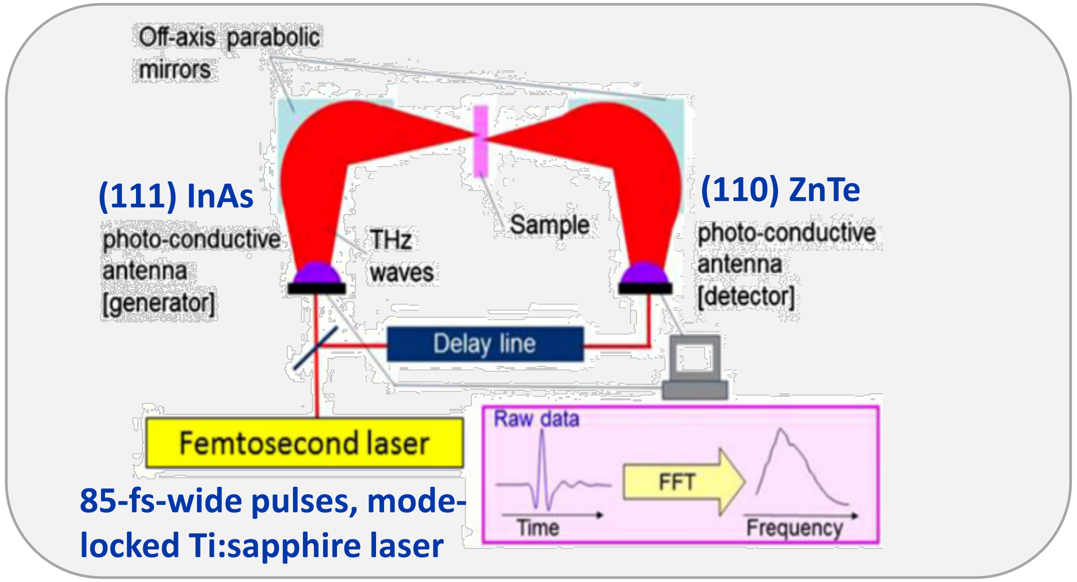
THz spectral dielectric constants of materials such as:

- superconductors
- toxic chemicals
- nonpolar/polar liquids
- vapors/gases
- semiconductors
  - bulk, thin film, and quantum-well structures

In this talk, we will concentrate on the THZ-TDS analysis of conductive nanocellulose based composites mixed together with PEDOT:PSS conductive polymer.

THz TIME-DOMAIN SPECTROSCOPY (THz-TDS)

THz waves *transmitted* through the sample at 298 K



Complex conductivity spectra can be achieved:

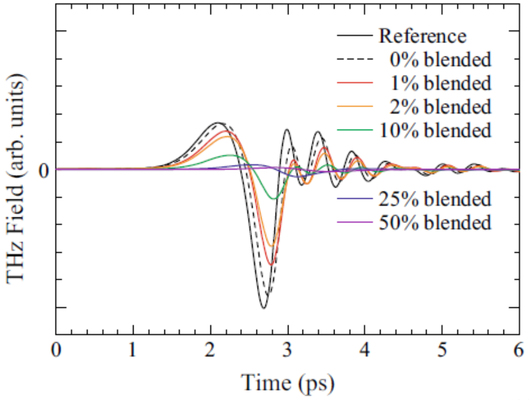
$$\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega),$$

where $\sigma_1(\omega)$ = conductive properties of carriers

$-\sigma_2(\omega)$ = dielectric properties of carriers

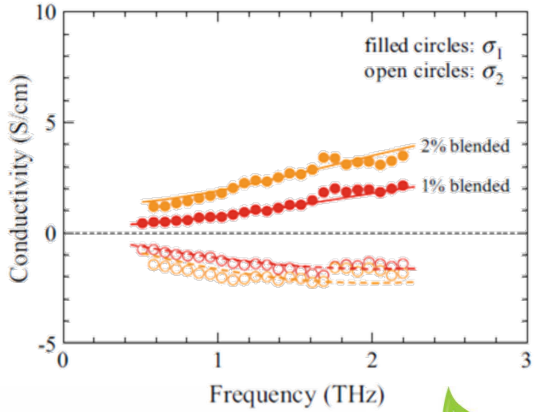
at a frequency of $\omega/2\pi$

Measured THz pulse

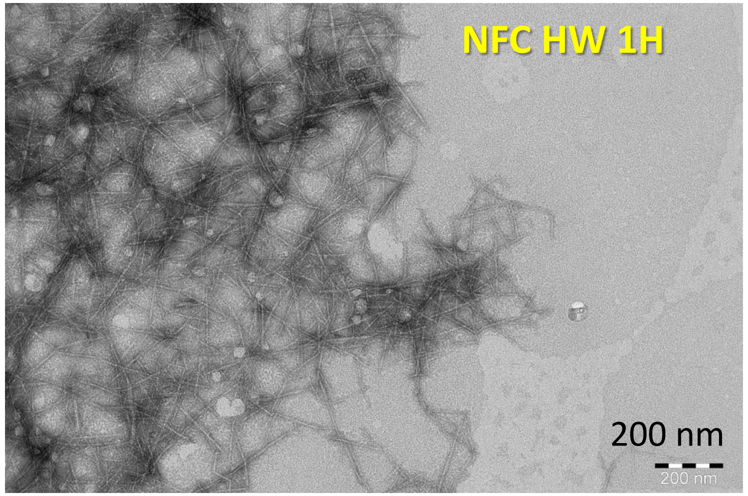


Fourier transform & Drude-Smith model

Complex conductivity



RAW MATERIALS AND THEIR PROCESSING



- **Cellulose nanofibers (CNF)** (Supplied by the South China University of Technology)
    - Hardwood (HW) – Bleached Eucalyptus Kraft Pulp (Votorantim Celulose Papel from Brazil)
- **Cellulose nanocrystals (CNC)** (aqueous dispersion from Melodea Ltd.)
- **PEDOT:PSS** (Organic conductive polymer used to impart conductivity to films, Clevios PH 500, Heraeus Holding, Germany)
- **Glycerol** (used as plasticizer, Sigma-Aldrich)

High pressure homogenization (2 000 bar, 2 times) with a chemical pretreatment (TEMPO, pH 10 – 11, 12 mmol/g, 3 hours reaction time) was used for obtaining NFC.

Hardwood NFC was obtained after 1 time and 2 times homogenization and named HW 1H and HW 2H.

PEDOT:PSS was blended together in six different dry weight percentages (0–50%) of PEDOT:PSS without/with the addition of glycerol.

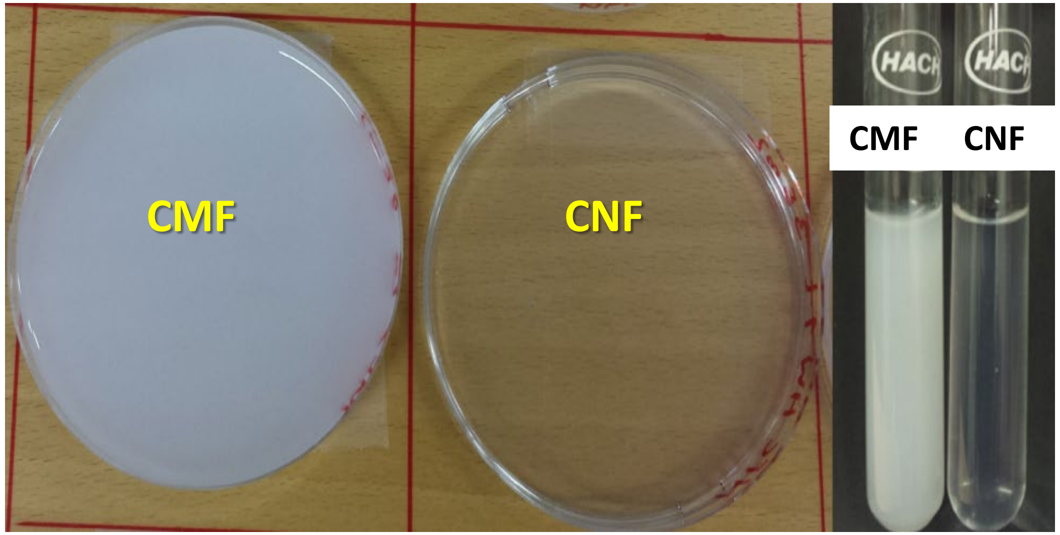
SAMPLE PREPARATION: FILM CASTING

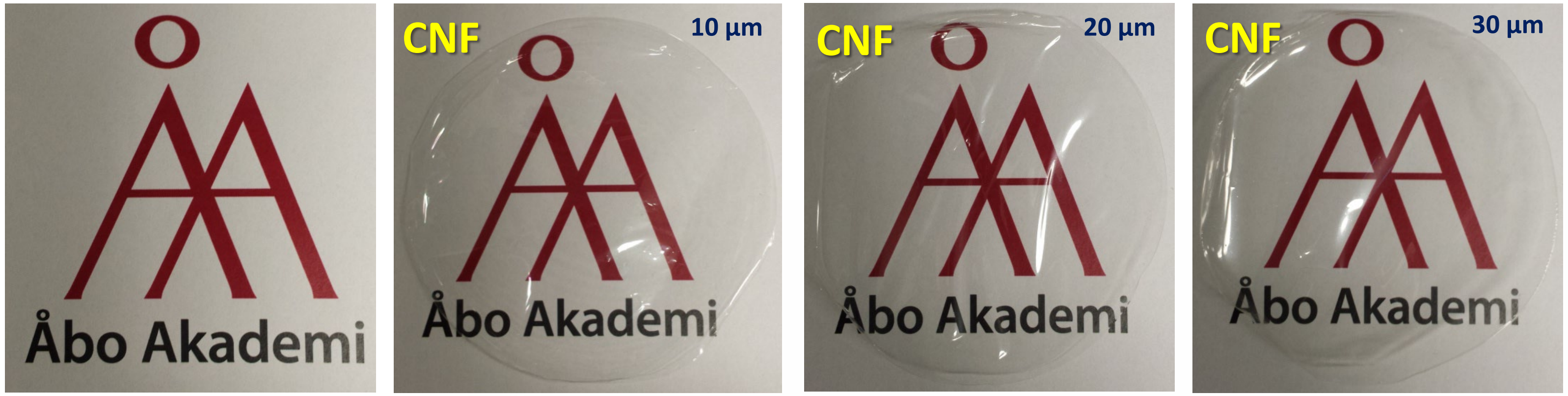
Each composite dispersion was diluted to a solids content of 0.20% and then cast on polystyrene Petri dishes (with a diameter of 8.5 cm) in a controlled atmosphere (temperature of 23°C, relative humidity of 50%).

Dried films were lifted off from the Petri dishes and thus obtained ***the free-standing samples***.

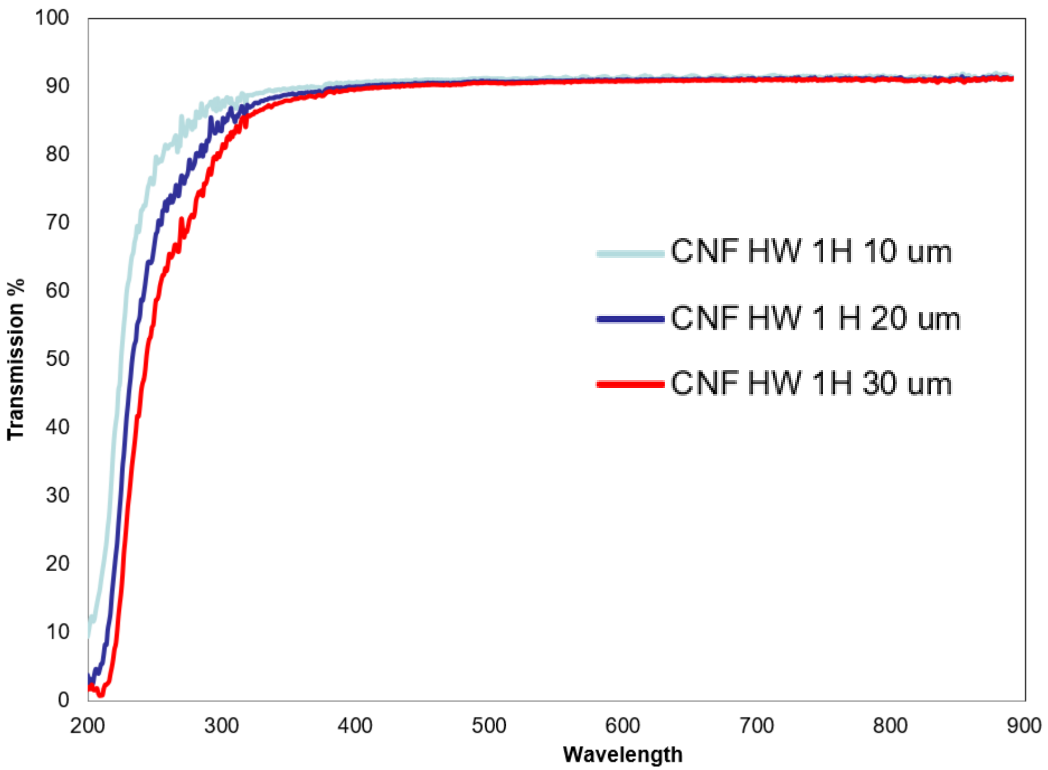
The thicknesses of the samples used for THz transmission measurements were approximately 20 μm:

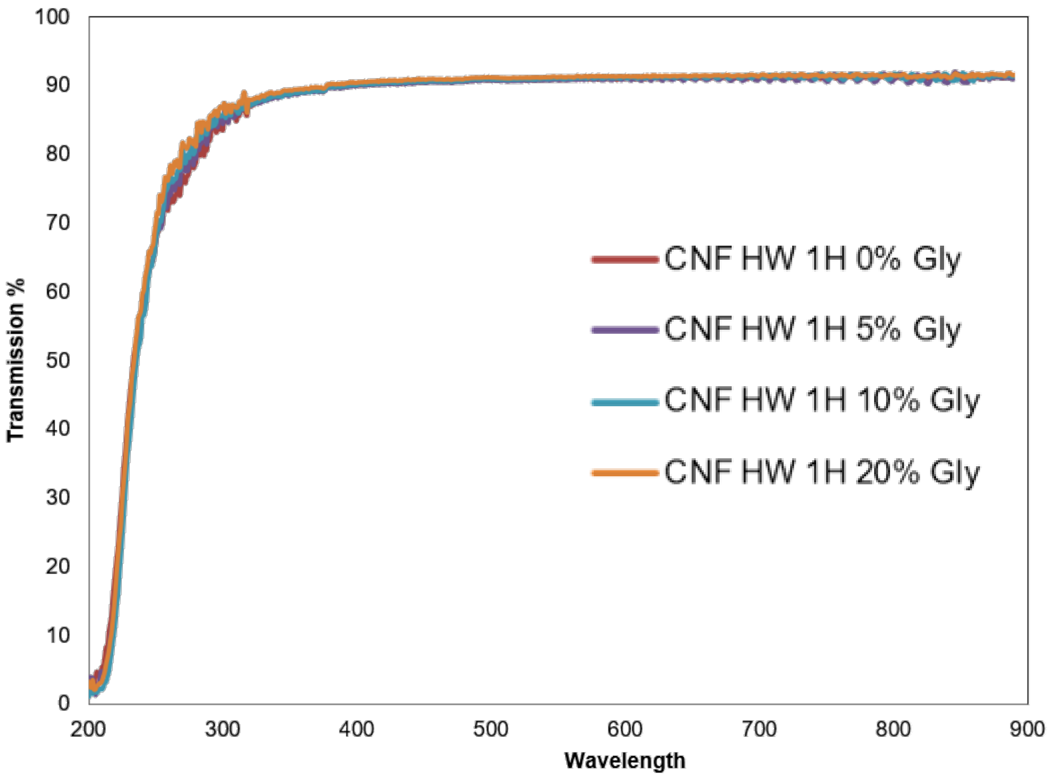
- 19–27 μm for the **CNF** series
- 19–21 μm for the **CNC** series
- 17–24 μm for the **CNC/G** series





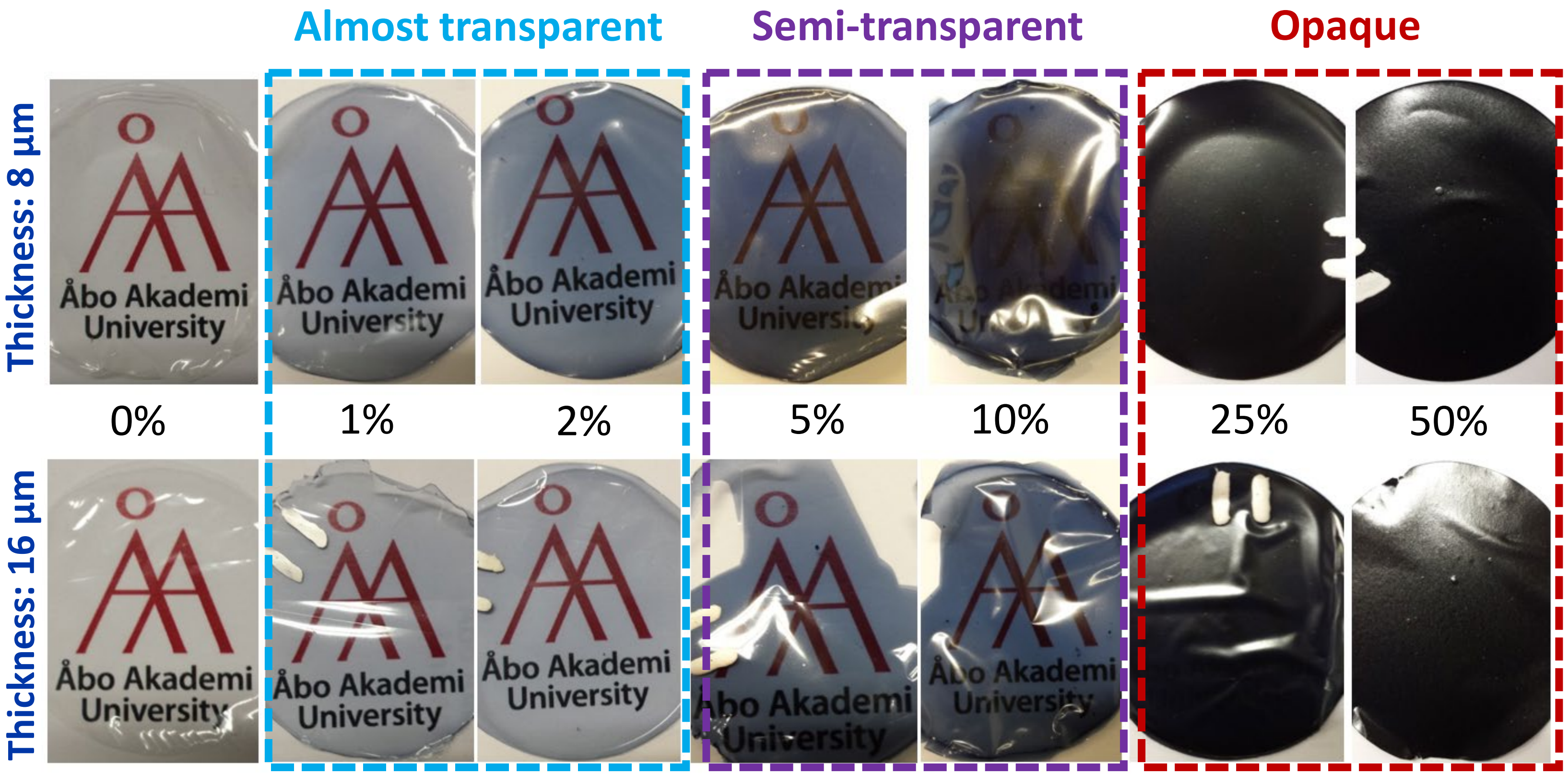
OPTICAL PROPERTIES OF CNF FILMS: EFFECT OF THICKNESS AND GLYCEROL ADDITION

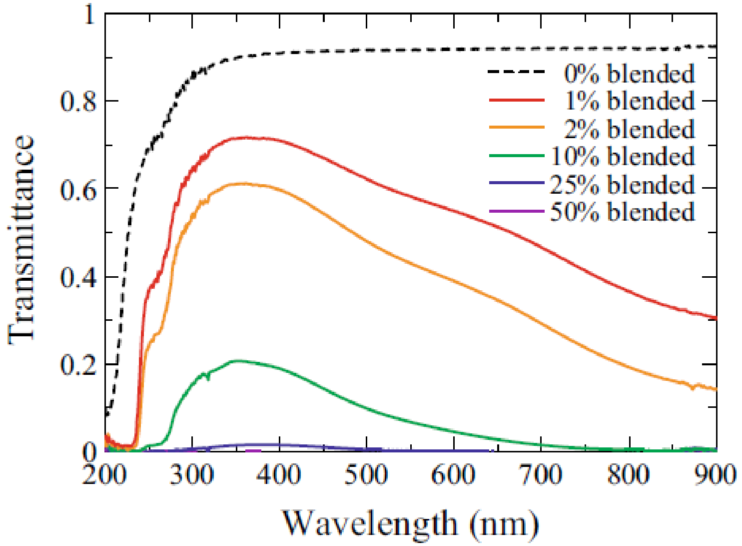




No significant effect on optical properties was observed in the visible range of CNF films independent of their thickness or the glycerol content.

OPTICAL PROTERTIES: PEDOT:PSS ON CNF FILMS



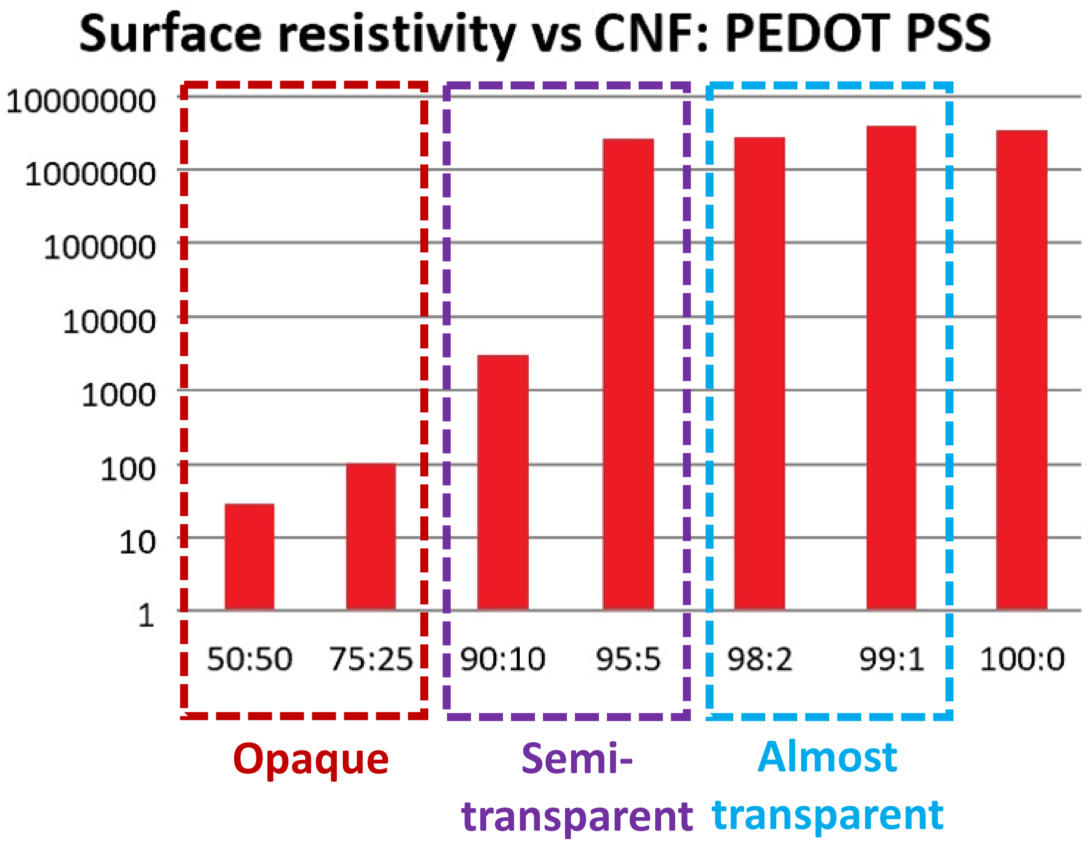


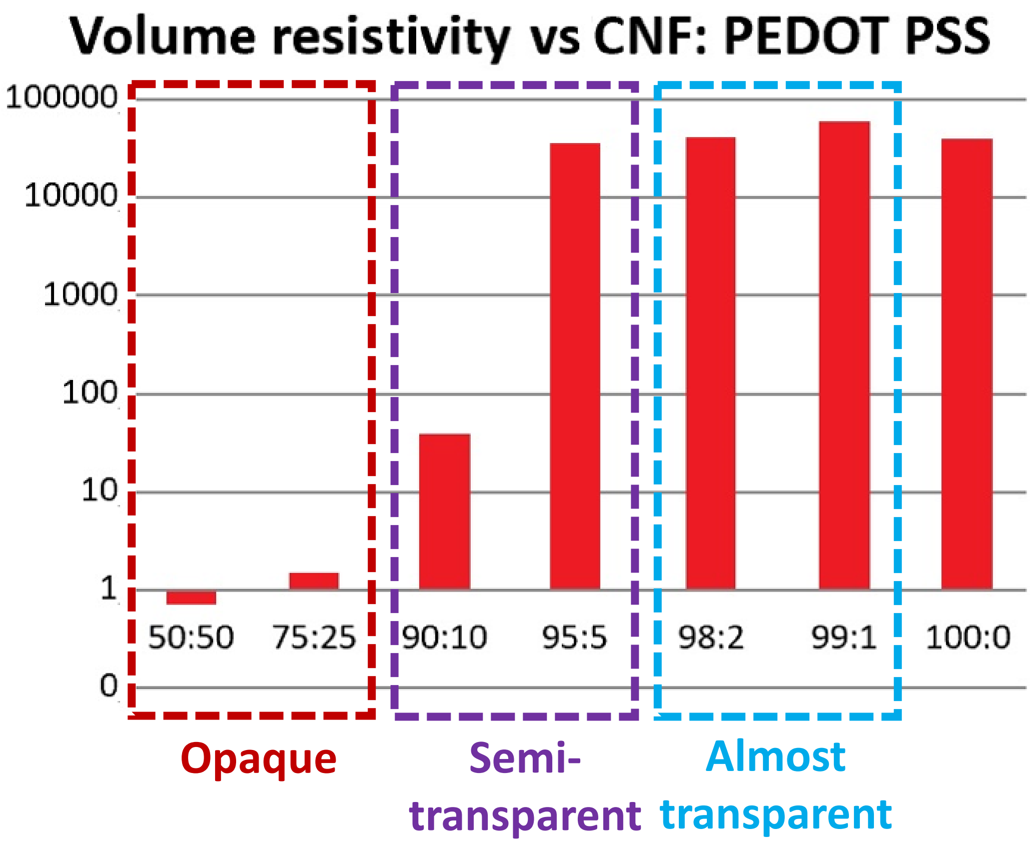
Addition of PEDOT:PSS had a significant effect on optical transparency of CNF composites:

- Almost transparent films with 1 and 2 wt.% of PEDOT:PSS
- Semi-transparent films with 5 and 10 wt.% of PEDOT:PSS
- Opaque films with 25 and 50 wt.% of PEDOT:PSS

T. Unuma *et al.* *Cellulose* **26**, 3247 (2019).

ELECTRICAL PROPERTIES: PEDOT:PSS ON CNF FILMS

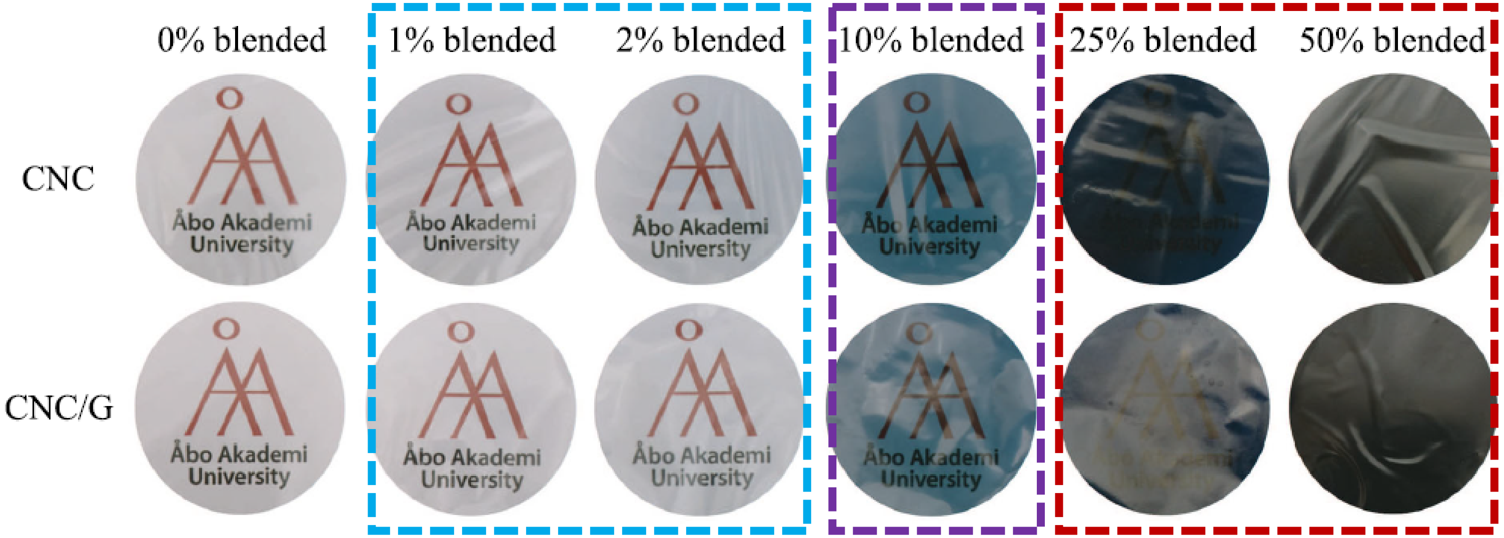


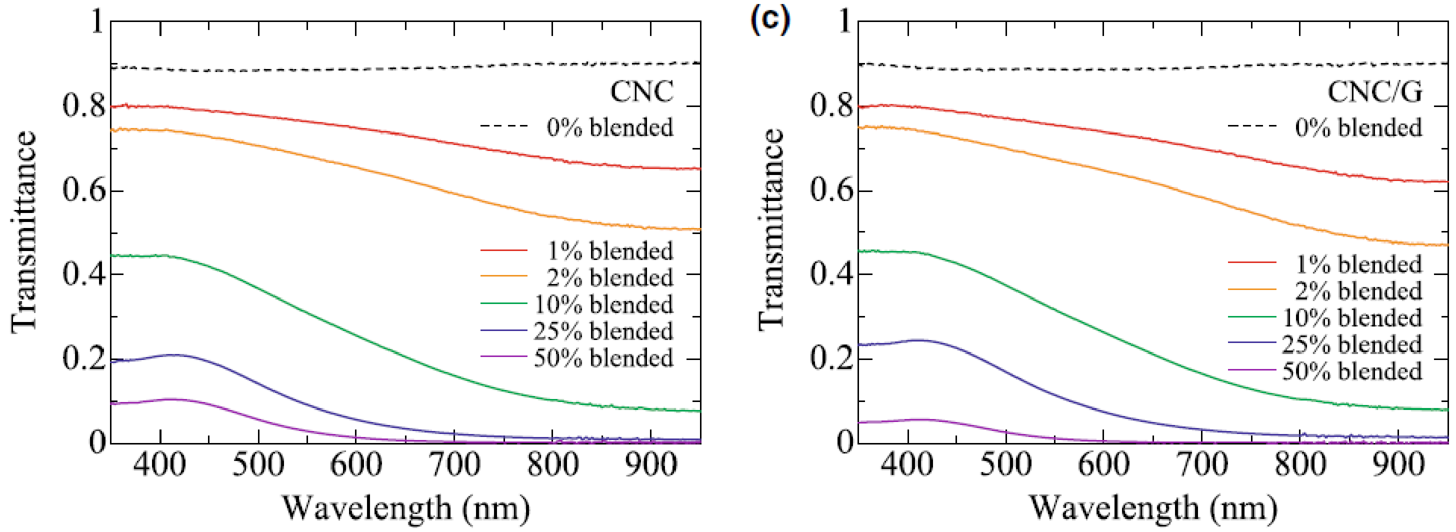


Addition of PEDOT:PSS has a significant effect on surface and volume resistivity of CNF composites :

- Almost transparent films (1 and 2 wt.%) are non-conductive
- Opaque films (25 and 50 wt.%) have good conductivity
- Semi-transparent films (5 and 10 wt.%) are in between conductive and insulating

OPTICAL PROTERTIES: PEDOT:PSS ON CNC





A similar observation to the **CNF** results i.e.

- Almost transparent films with 1 and 2 wt.% of PEDOT:PSS
- Semi-transparent films with 10 wt.% of PEDOT:PSS
- Opaque films with 25 and 50 wt.% of PEDOT:PSS

No significant effect of glycerol addition was found similar to the **CNF** films.

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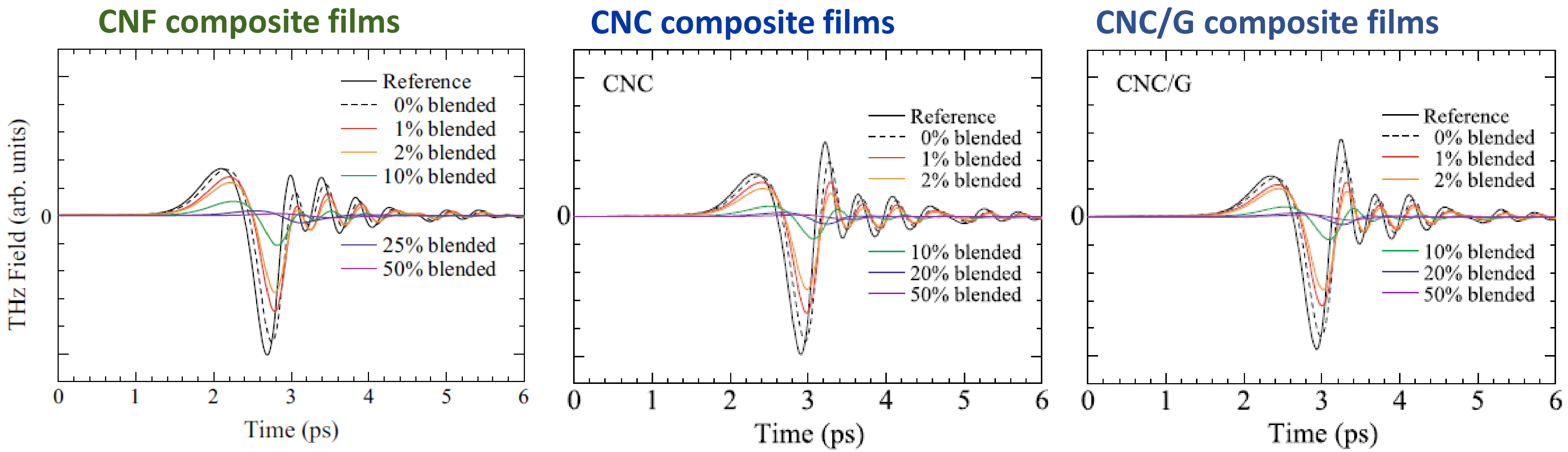
THz WAVEFORMS



Two main observations were found from all CNF/CNC/CNC/G – PEDOT:PSS composite films:

1. THz signals appeared with a systematic shift in time i.e. the velocity c/n of the THz waves (c: vacuum light velocity, n: refractive index) inside these composites decreased significantly as the PEDOT:PSS blending percentage was increased.
2. The amplitude decreased substantially with the PEDOT:PSS blending percentage, suggesting an increase in the absorption coefficient α of these composites.

Thickness variation had only a minor qualitative effect in these observed THz waveforms.

T. Unuma *et al.* *Cellulose* **26**, 3247 (2019).
T. Unuma *et al.* *Cellulose* **27**, 10019 (2020).

FOURIER TRANSFORM OF THz WAVEFORMS

Fourier transform of the measured THz waveforms was used to obtain complex transmission spectrum $\tilde{t}(\omega)$

$$\tilde{t} = \frac{4\tilde{n}}{(\tilde{n}+1)^2} e^{i\omega(\tilde{n}-1)d/c} \sum_l \left(\frac{\tilde{n}-1}{\tilde{n}+1}\right)^{2l} e^{i\omega 2l\tilde{n}d/c},$$

where l (= 0; 1; 2; . . .) is the integer numbering a pair of internal reflections up to l = 5. The complex refractive index spectra n(ω), whose imaginary parts are the extinction coefficient spectra associated with the absorption coefficient spectra α(ω) as follows:

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega) \qquad \alpha(\omega) = 2\omega\kappa(\omega)/c$$

Finally, the complex conductivity is obtained from the complex refractive index as follows:

$$\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$$

$$\sigma_1 = 2\omega\epsilon_0 n\kappa$$

$$\sigma_2 = \omega\epsilon_0(\kappa^2 - n^2 + \varepsilon_\infty)$$

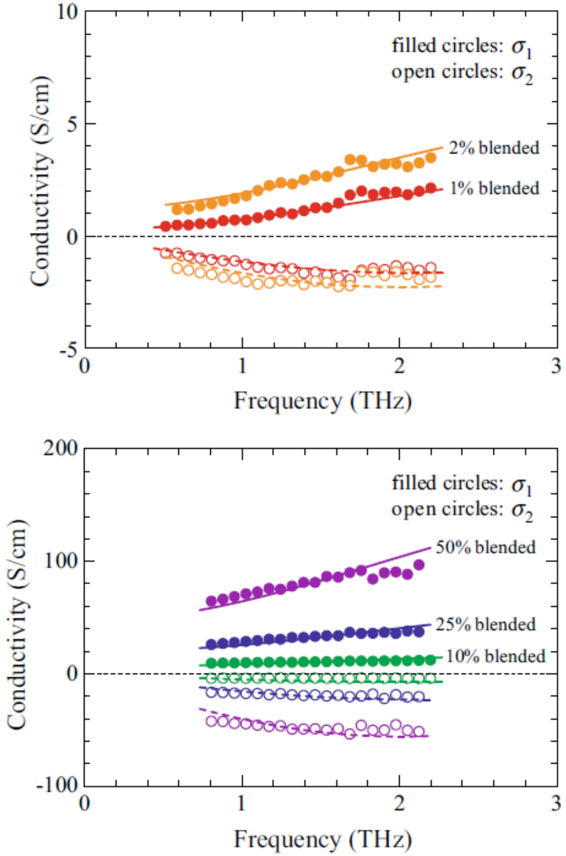
ϵ_0 = vacuum permittivity

ε_∞ = high-frequency background dielectric constant

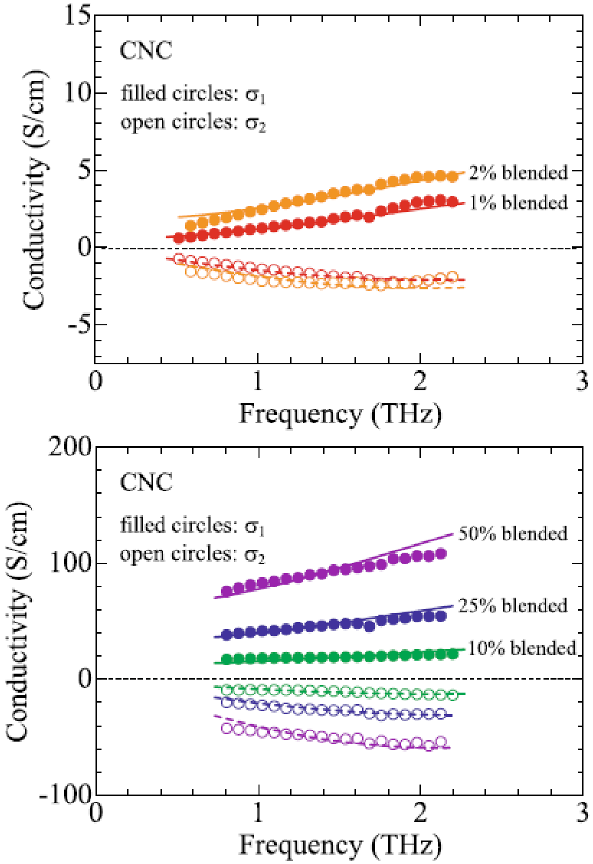
TAPPI NANO DIVISION

THz COMPLEX CONDUCTIVITIES

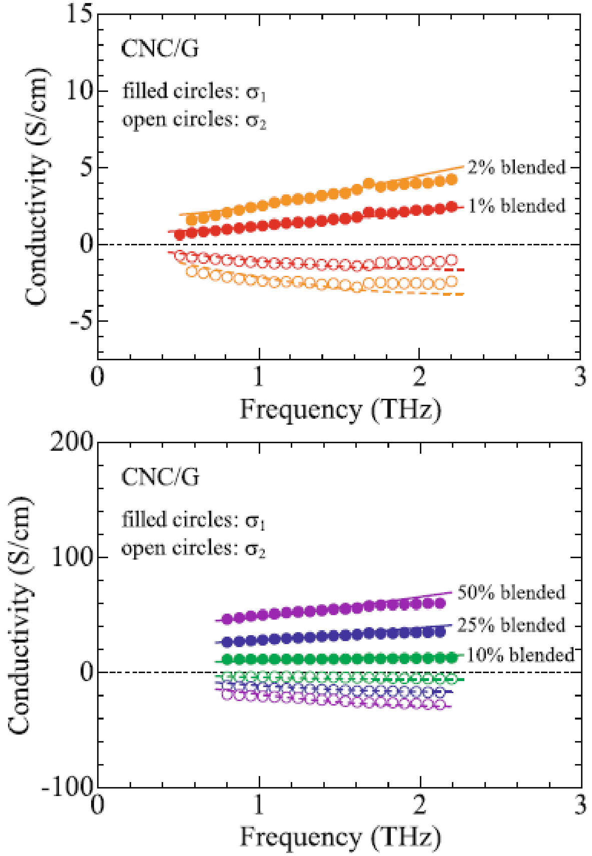
CNF composite films



CNC composite films



CNC/G composite films



Both the real parts σ_1 (filled circles) and the imaginary parts σ_2 (open circles) are larger for higher PEDOT:PSS blending percentages. A finite positive value of σ_1 and negative σ_2 values suggest that carriers in all these cellulose based composites have a ***partially localized nature***.

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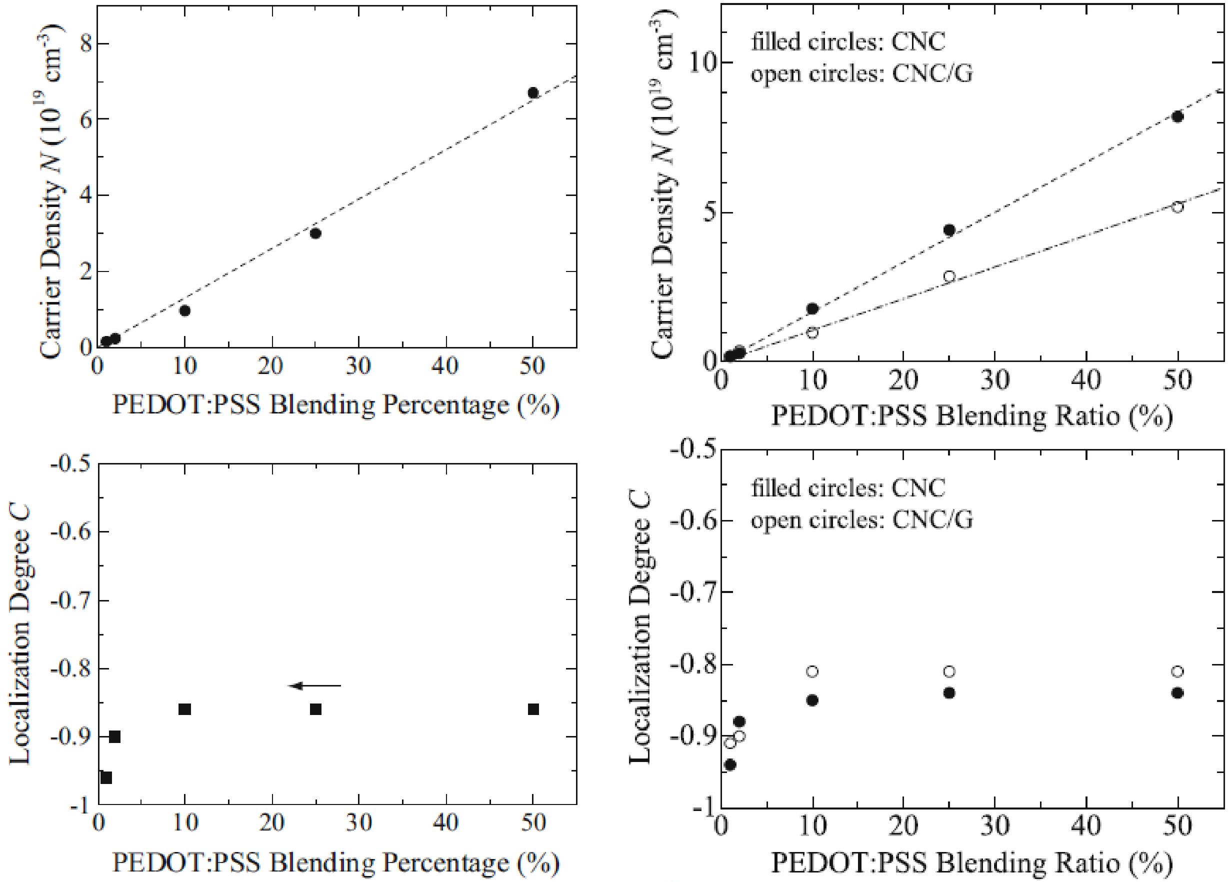
DRUDE-SMITH MODEL FOR PARTIALLY LOCALIZED CARRIERS

$$\tilde{\sigma}_{DS}(\omega) = \frac{Ne^2\tau/m^*}{1 - i\omega\tau}\left(1 + \frac{C}{1 - i\omega\tau}\right)$$

N = the volume density of carriers
τ = the momentum relaxation time
m* = the effective mass
C = the localization degree

C can change from a value of
-1 (for completely localized carriers) to
0 (for free carriers in the Drude model).



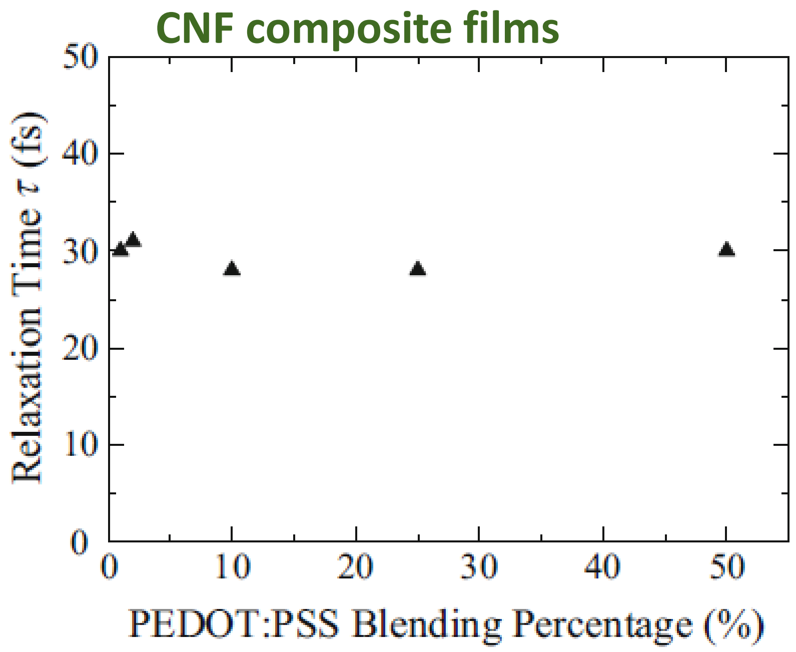
D-S estimates of DC conductivity

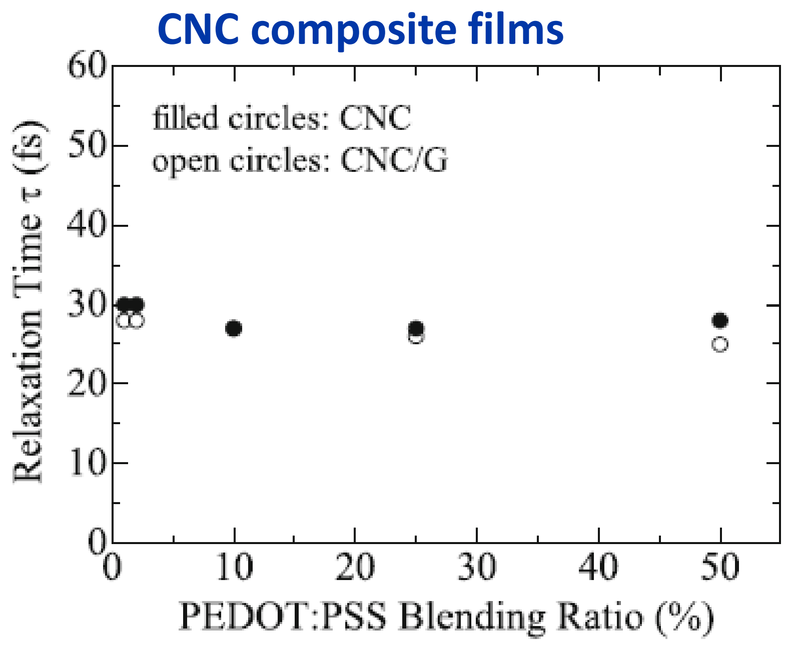
- CNF: $\sigma_{DS}(0)$ = 47 S/cm Four-probe: 45 S/cm
- CNC: $\sigma_{DS}(0)$ = 59 S/cm Four-probe: 51 S/cm
- CNC/G: $\sigma_{DS}(0)$ = 40 S/cm Four-probe: 46 S/cm

Drude-Smith model is valid from DC to THz frequencies!

N.V. Smith *Phys. Rev. B* **64**, 155 106 (2001).

DRUDE-SMITH MODEL: CARRIER RELAXATION TIME





A small variation was observed in the relaxation time between **CNF** and **CNC** & **CNC/G** composites:

- approximately 27 fs for **CNF** composites
- approximately 30 fs for **CNC** and **CNC/G** composites

Saturated values of C and the nearly constant values of s can be regarded as taking over the original nature of the carriers inherent in PEDOT:PSS.

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SUMMARY AND CONCLUSIONS

THz complex conductivity spectra of **CNF**/**CNC**/**CNC/G** based composite films with carriers induced by different blending ratios of PEDOT:PSS were acquired.

A ***partially localized nature*** of carriers was observed for all composites that were further analyzed using a Drude-Smith model.

These carriers became denser and less localized and kept a nearly constant relaxation time as the PEDOT:PSS blending ratio was increased.

These findings on the nanocellulose based composites can be applied to organic optoelectronics components, such as conductive or electrostatically dissipative flexible films with controlled semitransparency for both THz waves and visible light.

This work resulted in a generalized insight into the optoelectronic nature of carriers in nanocellulose based composites induced and modified by conductive organic materials in the THz region.

ACKNOWLEDGMENTS

Åbo Akademi University

Prof. Martti Toivakka
PhD Vinay Kumar
MSc Rajesh Koppolu

国立大学法人
長岡技術科学大学
Nagaoka University of Technology

Prof. Takeya Unuma
MSc Omou Kobayashi
MSc Shoya Kotaka

ACADEMY OF FINLAND

UNIVERSITY OF EASTERN FINLAND
Tampereen yliopisto
Tampere University
nSTAR
2022 – 2024
ACADEMY OF FINLAND

Academy of Finland funded
nSTAR research project (339 544)

PREI.N

Academy of Finland funded
Flagship for Photonics Research
and Innovation (**PREIN**)