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Engineering and Physical Sciences Research Council

MATERIALS & MANUFACTURING RESEARCH GROUP

Mechanical, Self-sensing, and Biological Characteristics of Additively Manufactured Multifunctional PEEK Composite Scaffolds

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Collaboration

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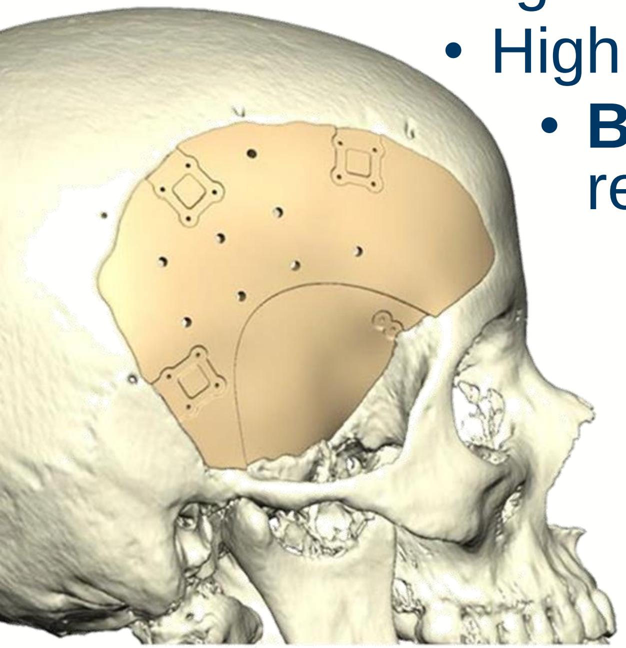
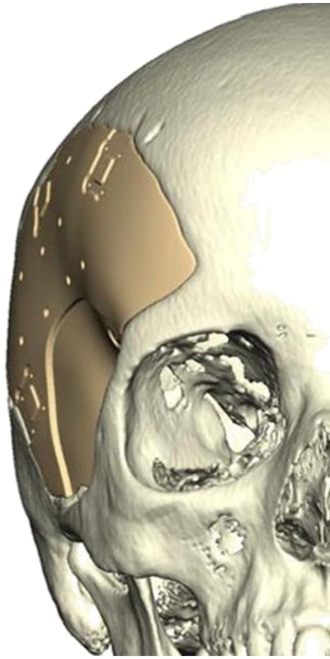
Outline

- Introduction
- Motivation and scope of the study
- Synthesis and characterization of feedstock
- Fused Filament Fabrication (FFF) of PEEK cellular composites
- Mechanical and Piezoresistive testing
- Biological characterization
- Conclusion and ongoing work

Introduction – Additive manufacturing (AM) of Orthopaedic PEEK implants

- Orthopaedic implants global market value $47.2 billion in 2022[2]
- Titanium alloys used as gold standard, with polyetheretherketone (PEEK) emerging for spinal-, joint-, trauma-, and arthroscopic implants
  - High-performance thermoplastic for a wide range of applications, including aerospace, automotive, and **biomedical**
    - High strength and stiffness properties
      - **Biocompatible**, chemically resistant, **bio-inert**, wear resistant, **radiolucent**
        - enables fabrication of biocompatible and mechanically stable patient-specific implants, utilising AM
        - AM via FFF of PEEK remains challenging as it processes above 343 °C

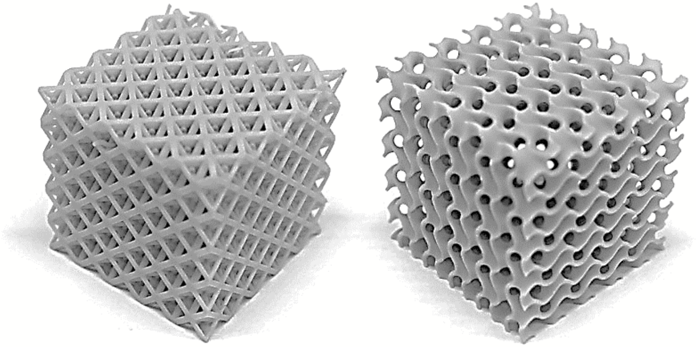


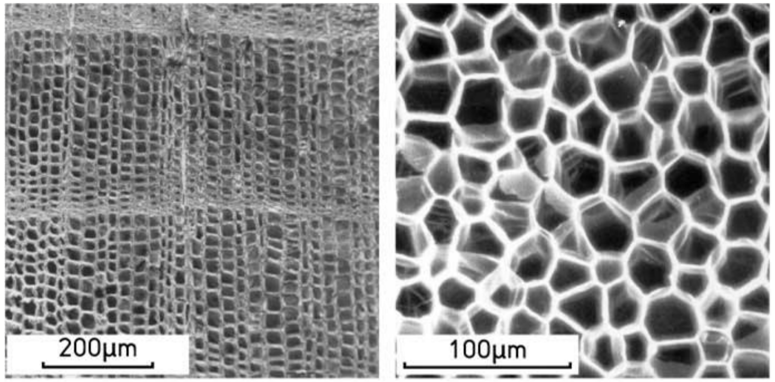


[1]O'Connor K et al., 2022 doi:10.1177/27325016211064340; [2]Orthopedic Implants Market Insights (2023)

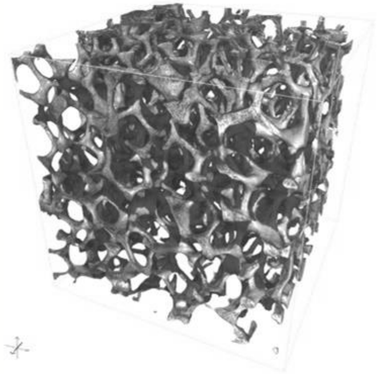
Introduction – Cellular structures

Periodic (fully ordered) | Random (disordered)





Gibson LJ et al, 2010



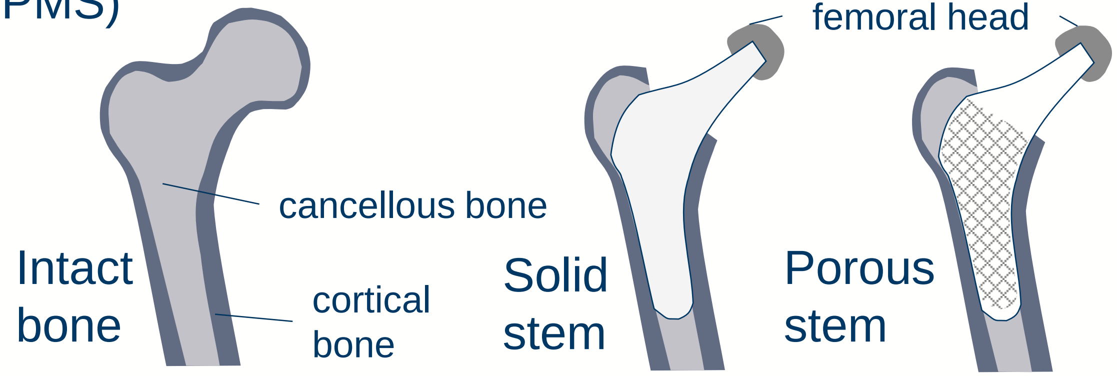
Geißendörfer et al, 2014

Open-cell, closed-cell, Triply periodic minimal surface (TPMS)

Natural foams, e.g. cedar, cork

Random foam

Graded porous implants to reduce stress-shielding and bone resorption



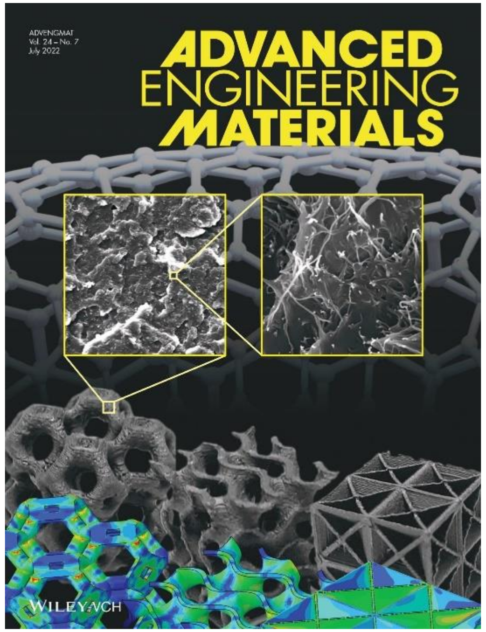
High surface area density (mm^2/mm^3) promotes favourable bone cell proliferation, attachment and rate of osseointegration

Introduction – self-sensing composites

- By integrating nanofillers like **carbon nanotubes** (CNTs) and **graphene nanoplatelets** (GNPs), polymers can be rendered electrically conductive, transforming them into self-sensing composites.
- Material itself is capable of sensing strain and damage – **piezoresistivity** can be leveraged
- In the early stages of deformation the gauge factor, *k*, is a measure of the materials sensitivity of the relative change in electrical resistance, *R*, to mechanical strain, ε, with

$$k = \frac{\Delta(\Delta R/R_0)}{\Delta L/L_0}$$

- Applications in structural health monitoring, condition-based maintenance, or smart materials



Cover art: J. Schneider

S. AlMahri, J. Schneider, A. Schiffer, S. Kumar, Piezoresistive sensing performance of multifunctional MWCNT/HDPE auxetic structures enabled by additive manufacturing, 2022, *Polymer Testing*
J. Ubaid, J. Schneider, V. S. Deshpande, B. L. Wardle, S. Kumar, Multifunctionality of Nanoengineered Self-Sensing Lattices Enabled by Additive Manufacturing, 2022, *Advanced Engineering Materials*

Aim of the work

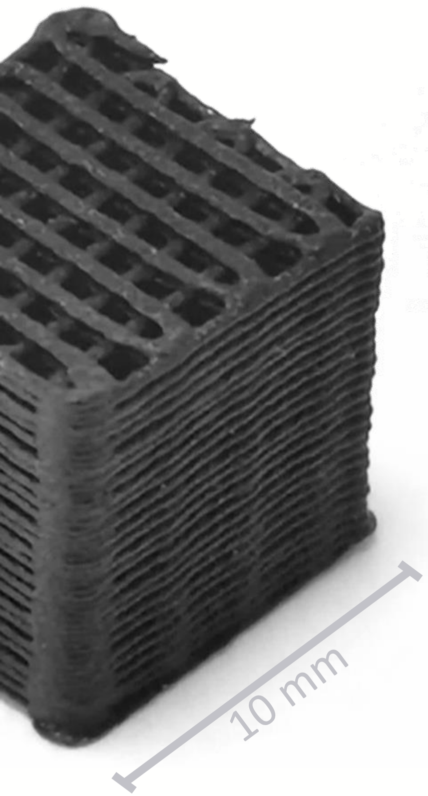
i. Development of novel nanomodified PEEK composites:
   - PEEK (neat), PEEK/CNT 6 weight percent (wt.%), PEEK/CNT/GNP 2×2.5 wt.%, PEEK/GNP 5 wt.%

ii. Modelling and 3D printing of PEEK cellular composites
   - Porosity: 63%, 56%, 41%

iii. Assessment of mechanical and piezoresistive performance of cellular scaffolds under compressive loading

iv. Analysis of surface characteristics of scaffolds

v. Assessment of *in vitro* biological response of 3D printed scaffolds of PEEK nanocomposites



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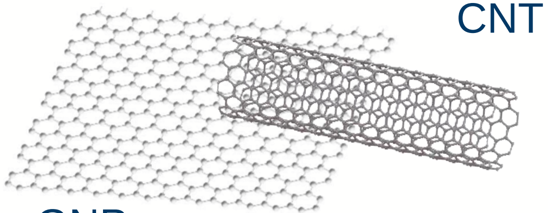
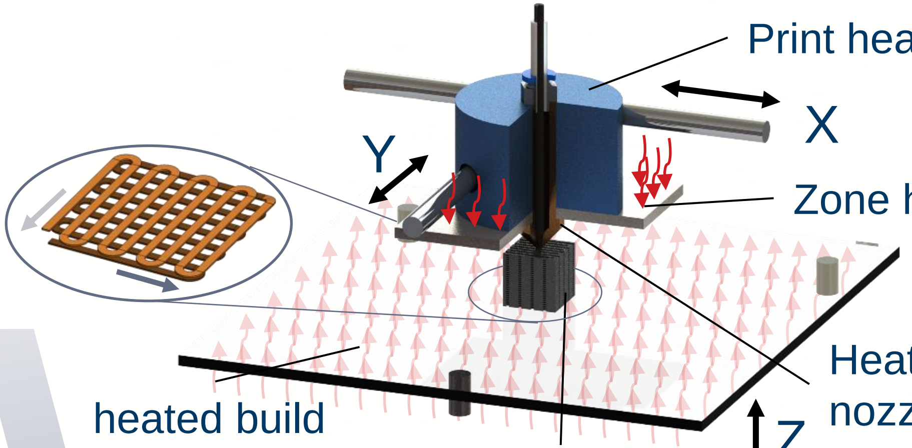
An Overview



PEEK

Filament Extrusion

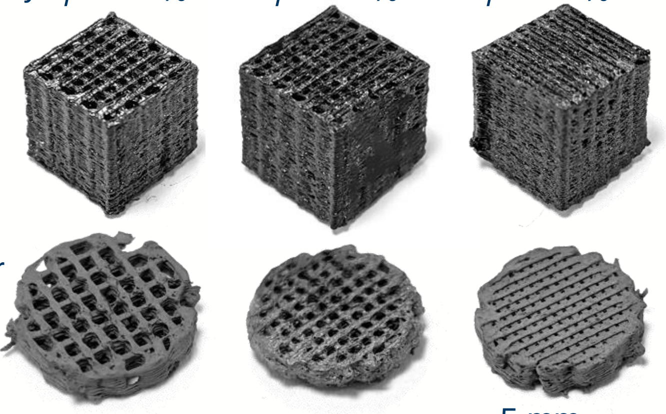


Pore size: 720 µm 470 µm 200 µm

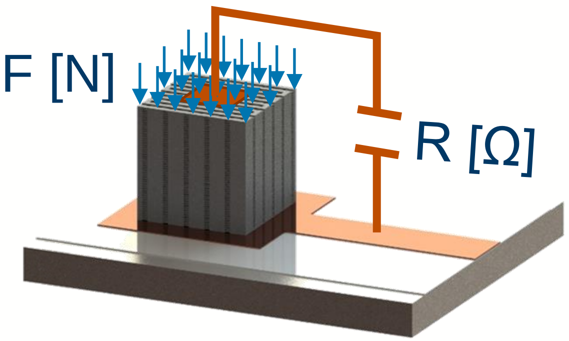
Relative density: $\bar{\rho} = 46\%$ $\bar{\rho} = 55\%$ $\bar{\rho} = 73\%$

Scaffolds for mechanical tests

Scaffolds for biomedical tests



Fused Filament Fabrication (FFF)



Compression Testing

Biological Characterisation

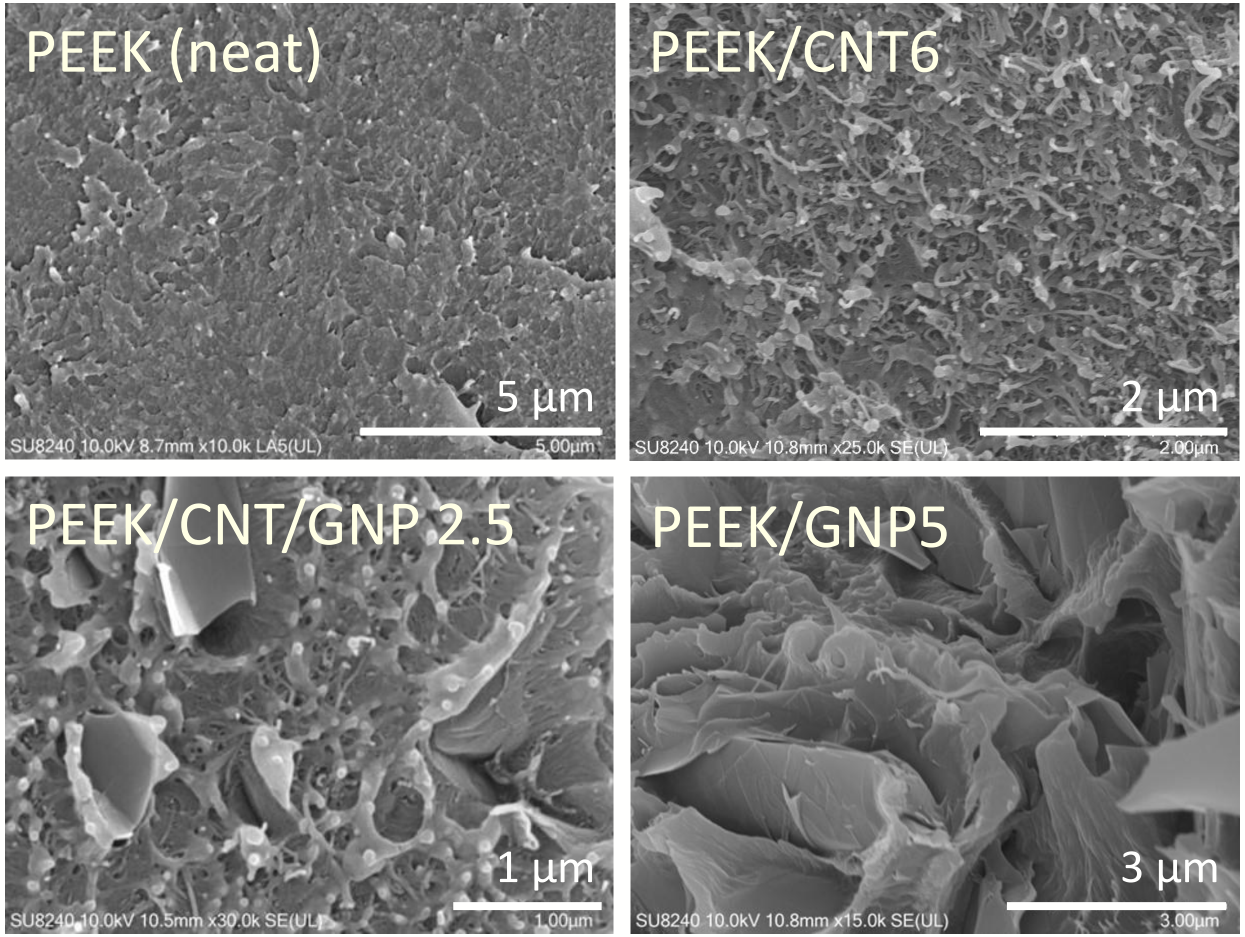
Results & Discussion

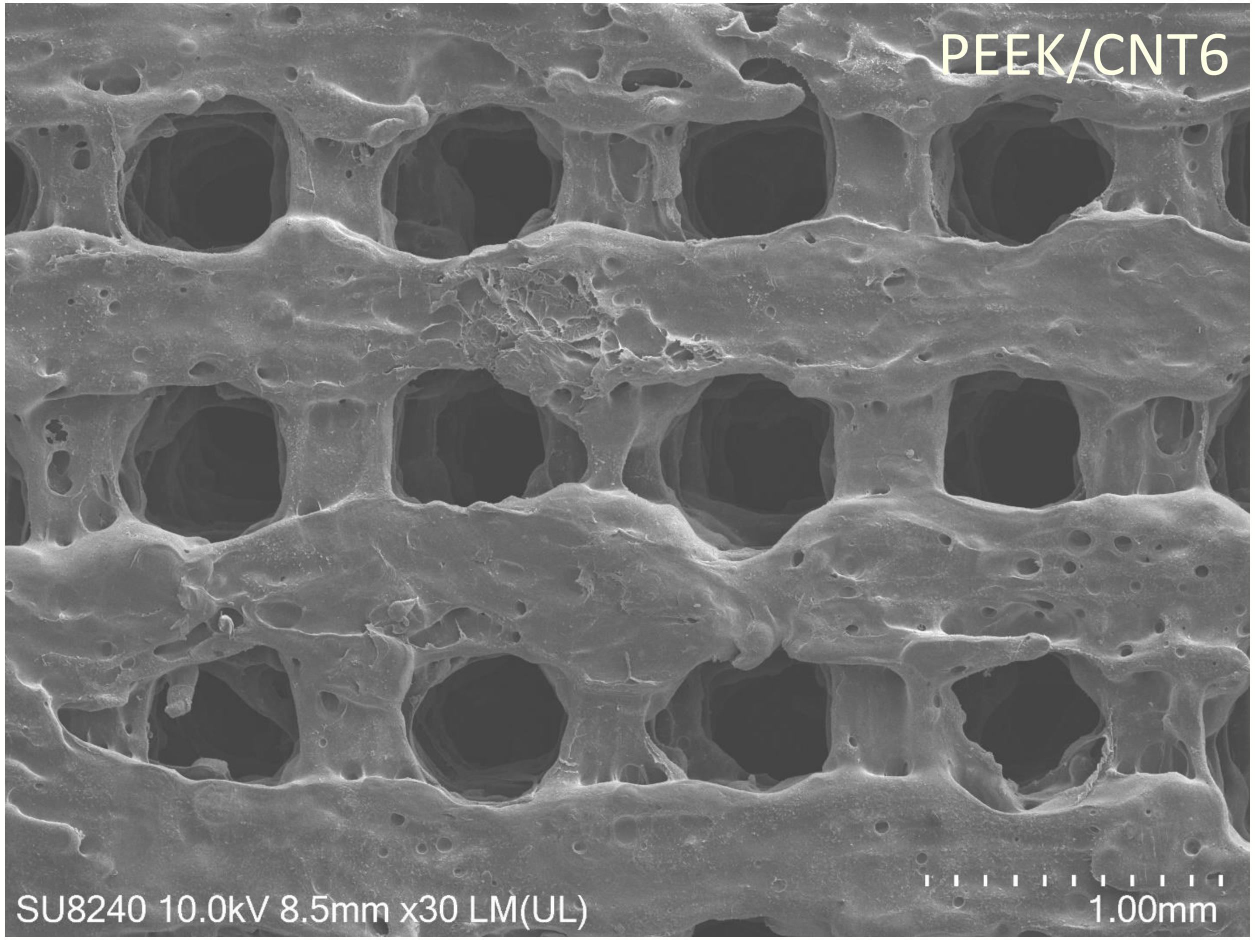
a) Mechanical and piezoresistive performance evaluation through
   I. Quasi-static compression testing up to densification
   II. Quasi-static cyclic compression testing, strain-controlled ($\Delta\varepsilon = 3\%$ with $\varepsilon_{max} = 5\%$)

b) Biological characterisation
   I. Surface modification through sulfonation
   II. In *vitro* **assays for cytotoxicity**, **cell proliferation** and **cell differentiation** were performed to assess the influence of scaffold material and porosity on bone cell precursors.

Cell Seeding and Culture	Viability Assay	Proliferation Assay	Alkaline Phosphatase Assay
MC3T3-E1 (murine osteoblast precursors) cultured over 14 days. Samples analysed on 1st, 7th and 14th day	Indicates metabolic activity of cells, denotes percentage of cells alive in presence of scaffolds, evaluates cytotoxicity	DNA quantification determines rate of cell multiplication in presence of scaffolds	Cell differentiation marker, indicates mature bone cell formation, can be used to map bone tissue regeneration

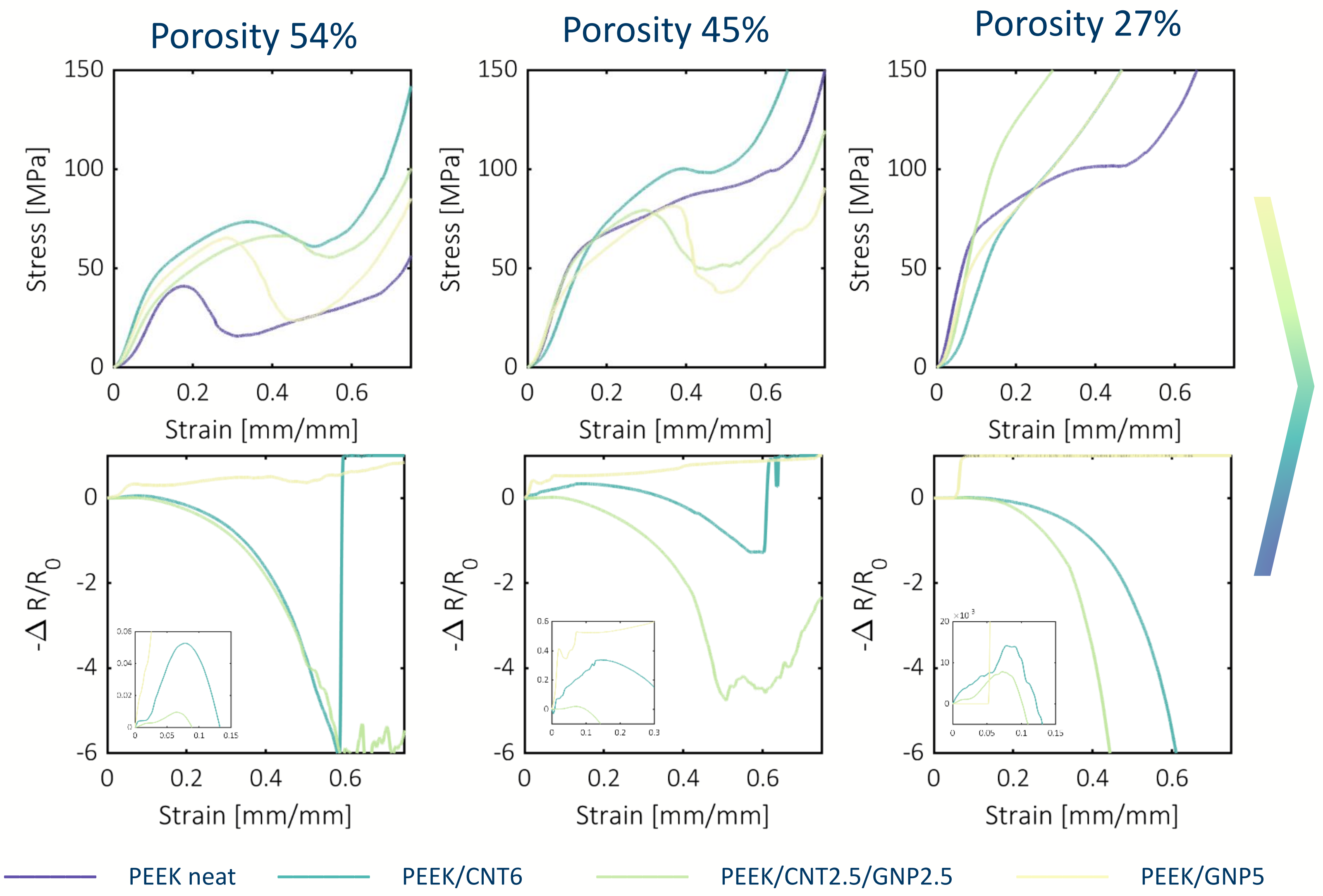
SEM imaging of cryogenically fractured surfaces/ 3D-printed lattice





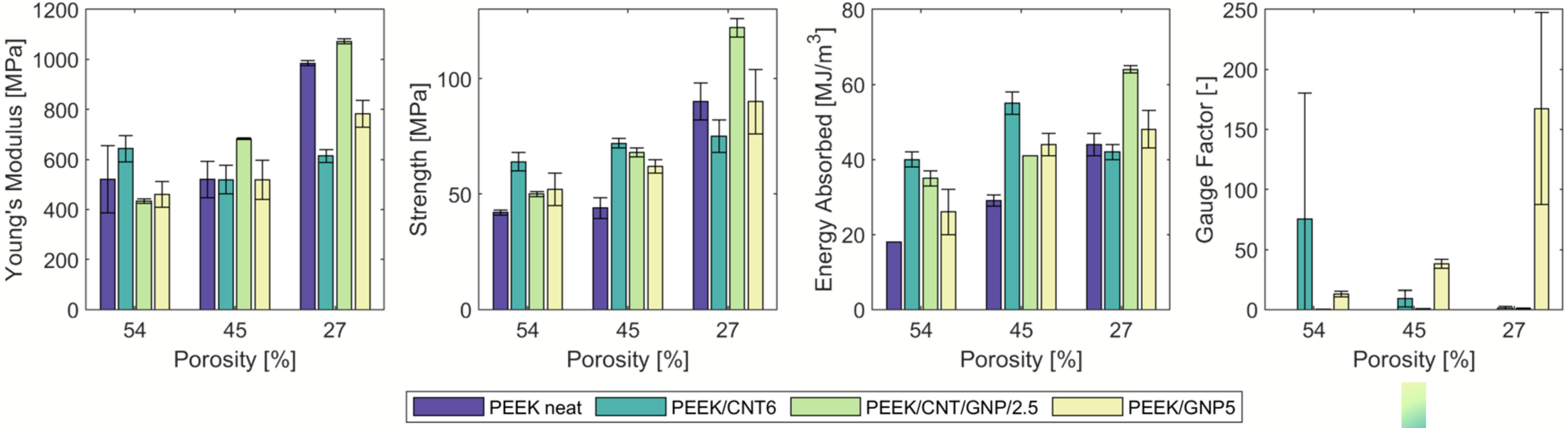
Presence and uniform dispersion of CNTs/GNPs in PEEK matrix

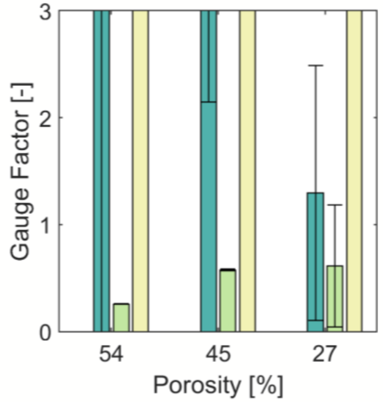
Mechanical and Piezoresistive characteristics under quasi-static compression: 3D printed scaffolds



- Stress-Strain response dictated by 3 regimes: linear elastic, plastic and densification
- Corresponding piezoresistive regimes:
- Resistance decreases initially until yielding of the material (improvement of conductive paths), and then increases up to densification regime (disruption of conductive paths due to crack formation) - composites with CNTs
- Resistance decreases steadily until densification for PEEK/GNP5 composites (becomes fully conductive)
- Collapse of ligaments govern piezo-resistance

Mechanical and Piezoelectric testing (QS)





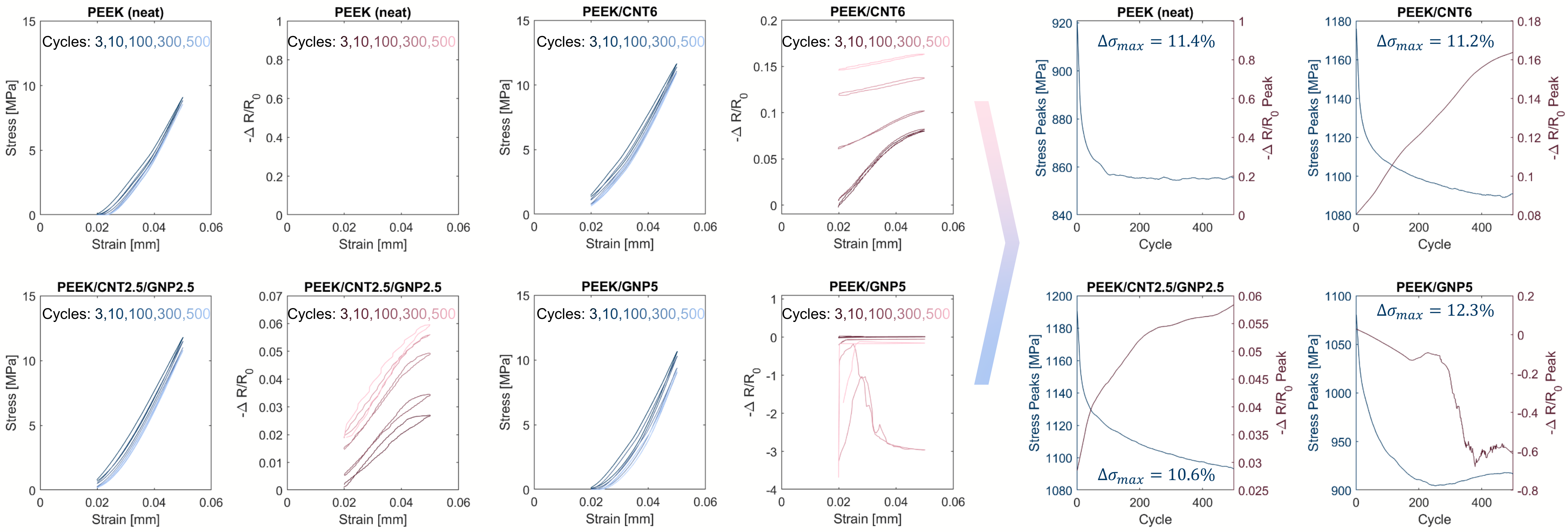
Mechanical performance increases with decreasing porosity

Decreasing piezoresistive sensitivity for PEEK/CNT6

Increasing piezoresistive sensitivity for PEEK/GNP5

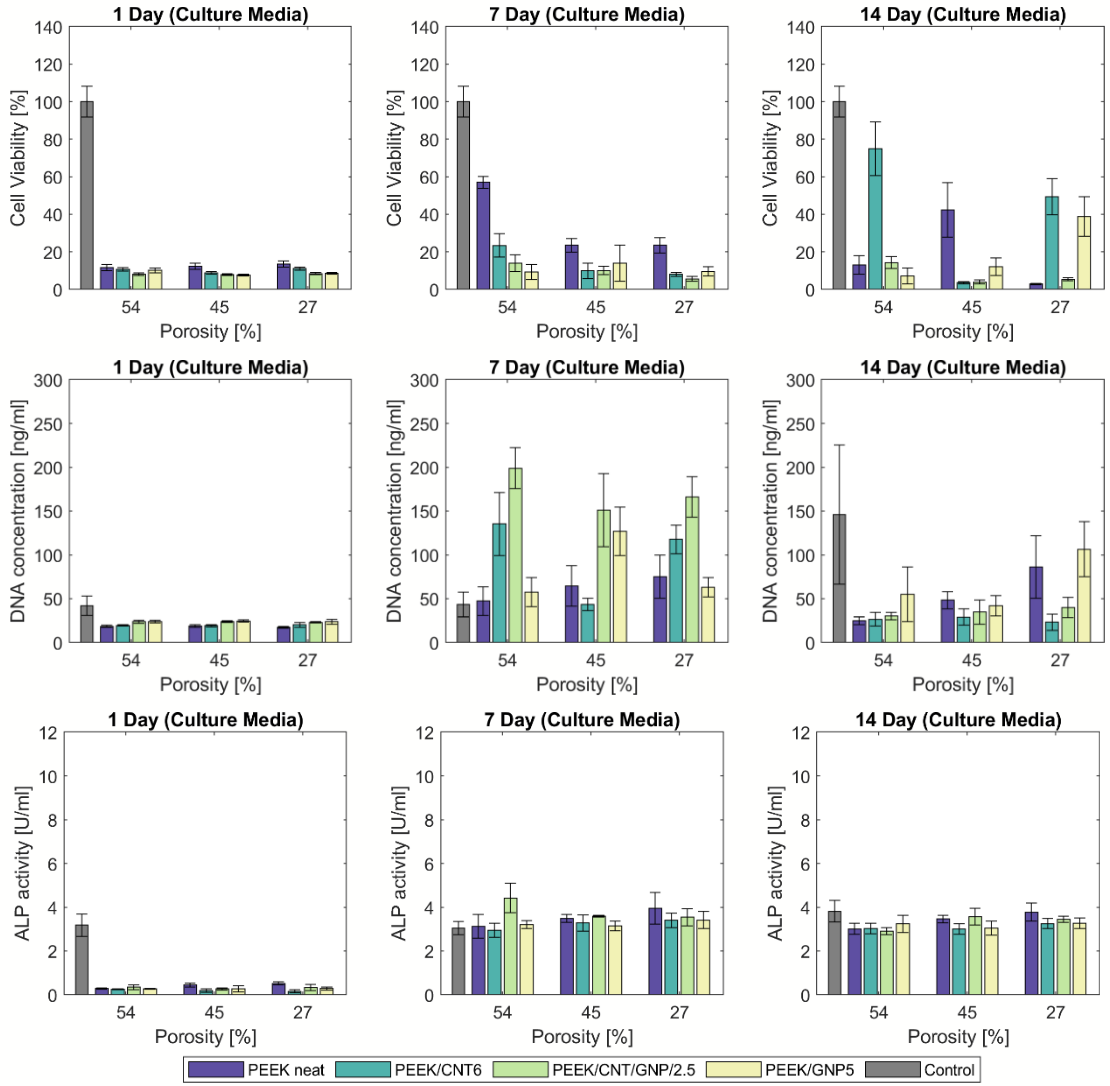
Low piezoresistive sensitivity for PEEK/CNT/GNP2.5

Mechanical and Piezoresistive behaviour under quasi-static cyclic compression: 3D printed scaffolds



$\Delta\varepsilon = 3\%$, $\varepsilon_{max} = 5\%$, Cycle count: 500 → approaching fatigue limit at 500 cycles

Results: Biological characterization



- Percentage cell viability, measured from fluorescence-based resazurin assay; cellular metabolism reaches a peak specific to the material and geometry
- Scaffolds support cell survival in selected cases
- Cell proliferation, determined by DNA quantification; DNA content reaches an overall maxima by day 7
- Favourable cell proliferation observed in PEEK/CNT/GNP/2.5 on day 7
- Elevated ALP expression observed consistently through days 7 to 14; indicates successful cell differentiation in presence of scaffolds

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Conclusions and ongoing work

- Successfully fabricated architected PEEK nanocomposite scaffolds with micro-scale features using in-house nanoengineered feedstocks comprising CNTs and/or GNPs
- The tuneable self-sensing and mechanical performance of PEEK composite lattices were experimentally demonstrated by varying their architectural parameters in addition to the filler content/type with a particular focus on strain and damage sensing.
- Successful cell survival, proliferation and cell differentiation observed in scaffolds over a 14-day span of cell culture under *in vitro* conditions.
- Further *in vitro* analytical procedures can be explored to visualize cell behavior in the scaffolds in real-time; Can enable prediction of their biological potential *in vivo*
- Finite element studies are being carried out to predict the mechanical and piezoresistive performance and to develop a predictive capability

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Thank you.

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References

- Slide 4 - Cranial implant images: O'Connor K et al., 2022; doi:10.1177/27325016211064340
- Slide 4 - Orthopaedic Implants Market Insights | Segments | Forecast- 2032, Allied Market Research. (n.d.). https://www.alliedmarketresearch.com/orthopedic-implants-market (accessed February 24, 2023)
- Slide 5 - Nature foam image: https://lornagibson.org/research.html; *Cellular materials in nature: cedar (left), cork (right)* From Gibson LJ, Ashby MF and Harley BA (2010) Cellular Materials in Nature and Medicine. Cambridge University Press.
- Slide 5 - Stochastic foam image: Geißendörfer et al, 2014; https://doi.org/10.1016/j.probengmech.2014.06.006