



UNIVERSITY OF
LIVERPOOL

MATERIALS
INNOVATION
FACTORY

Designing colloidal formulations and bespoke rheological tests for 3D printing

Andrew Corker, Dr Henry Ng, Prof Robert J Poole & Dr Esther García-Tuñón



FORMATIVE FORMULATION

**Formative Formulation: a technical meeting for early career formulation scientists in
industry and academia**

*Maxwell Centre, University of Cambridge, JJ Thomson Ave, CB30HE
18th March 2019*



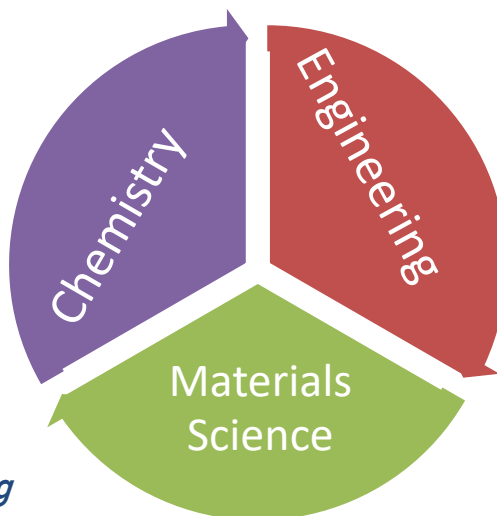
The Leverhulme Trust



Engineering and Physical Sciences
Research Council



Fundación Barrié



UNIVERSITY OF
LIVERPOOL

Dr. Esther García-Tuñón

Lecturer in Materials Science and Engineering

School of Engineering and Materials Innovation Factory

Esther.GTunon@liverpool.ac.uk

MATERIALS
INNOVATION
FACTORY

<https://egtunongroup.com/>



@esthergtb

TUÑÓN GROUP

Colloidal Processing and Rheology Research @UoL

TEAM



Andrew Corker
(Second year PhD student)



Emma Jones
(First year PhD student)



Alice Brettie
(First year PhD student)

Open PhD opportunities



'Inside' personal care products:
developing characterisation protocols
combining microfluidics and advanced
imaging techniques ◯

University of Liverpool | School of Engineering | Liverpool | United Kingdom

Dr E. E. T. Tuñón
Dr M. J. Martínez

Tuesday, April 22, 2014

Multiscale Quasiperiodic Metamaterials ◯

University of Liverpool | School of Engineering | Liverpool | United Kingdom

Dr E. E. T. Tuñón
Dr M. J. Martínez

Tuesday, April 22, 2014

ICASE



Project with
Physics Department

Synthesis of responsive surfactants.
Formulation & colloidal processing.
Rheology of complex fluids.
3D printing of advanced materials.

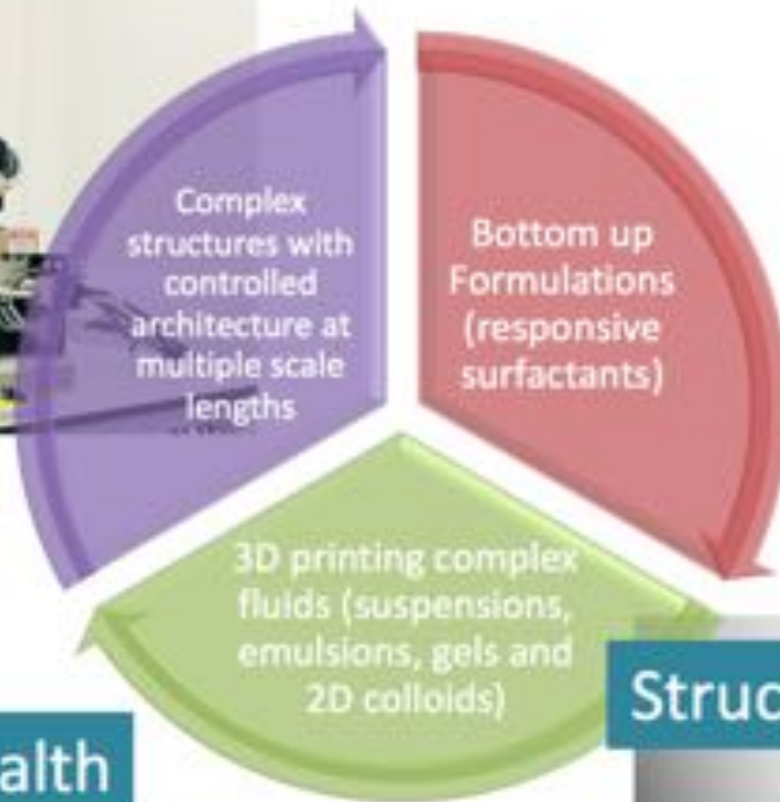
Research overview

[No Title]

Engineering complex fluids



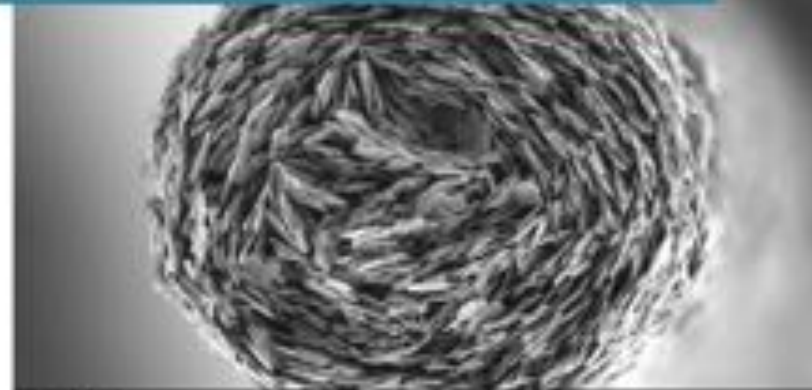
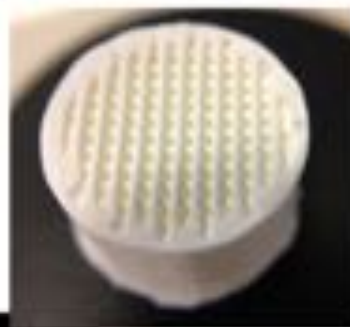
UNIVERSITY OF
LIVERPOOL



Energy

Structural Applications

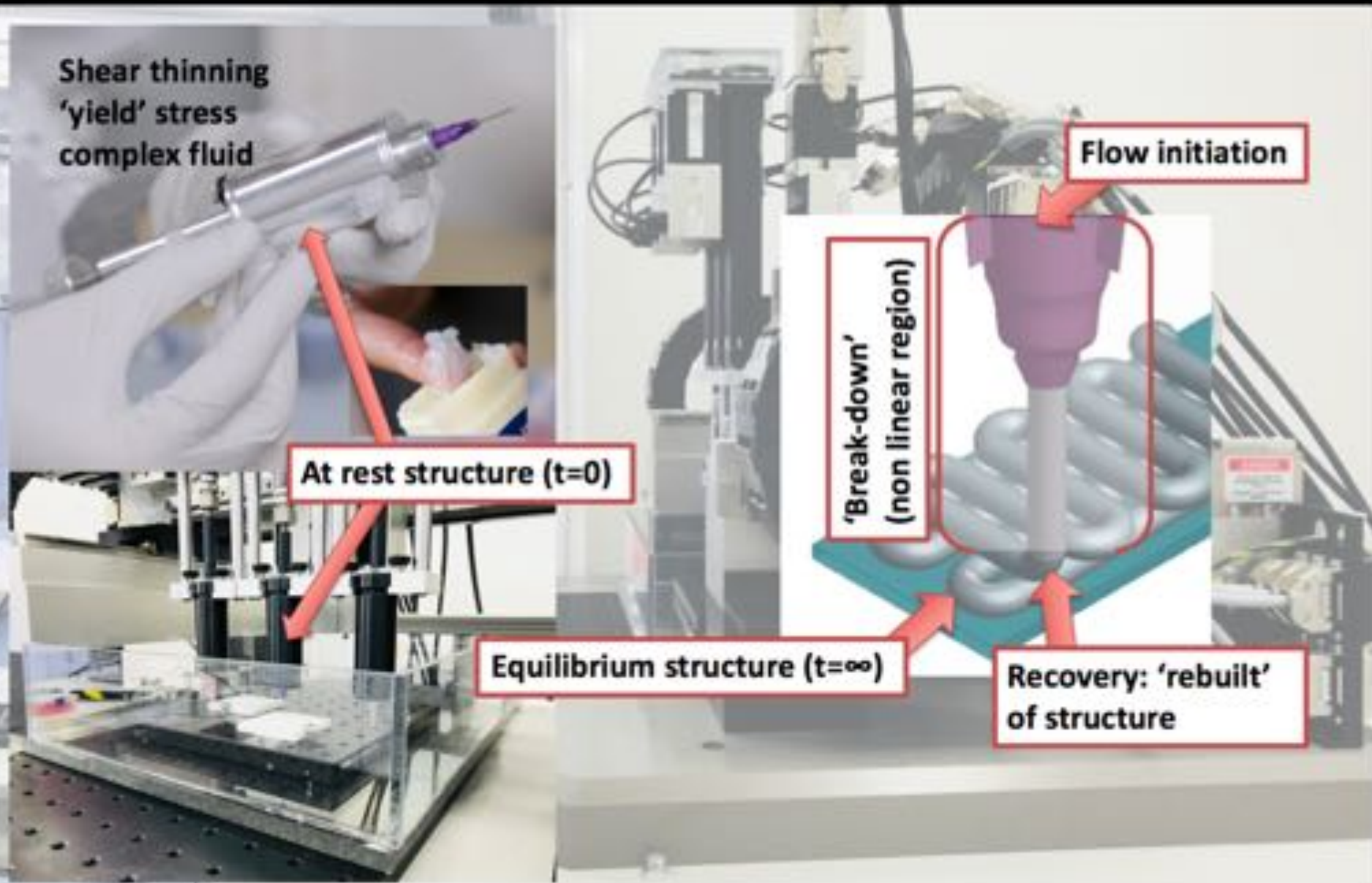
Health



1 μm

30 μm

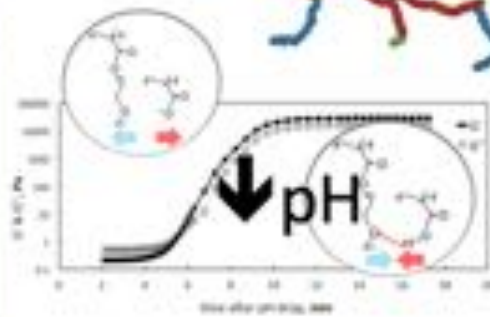
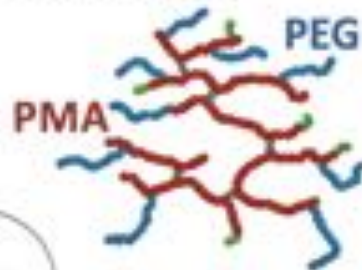
DIW: Rheological demands and '*printability*'



Engineering formulations for DIW

**pH responsive
surfactants**

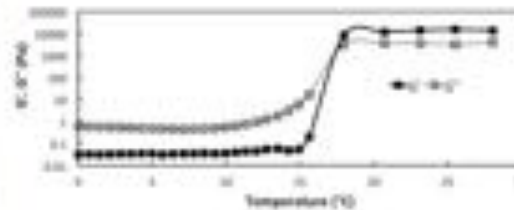
BCS
Branched
Copolymer
Surfactant



Printing in Three Dimensions with Graphene

James David Smith, 4 James Way, 2nd Floor, Boston City School District
Boston, MA 02118. James Christopher Smith, American Legion and Edward J. ...

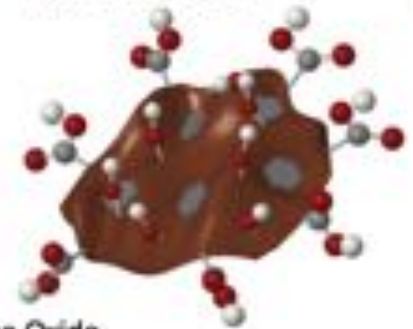
Thermo-responsive hydrogels



ES-07L

Multilayered 3D Printing of Graphene-Based Electrodes for Supercapacitor Energy Storage Using Thermoplastic Ink

2D colloids



GO 
Graphene Oxide

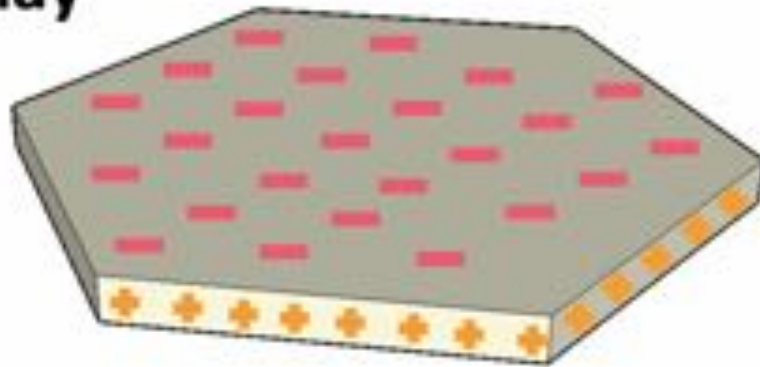
APPENDIX

Graphene Oxide: An All-in-One Processing Additive for 3D Printing

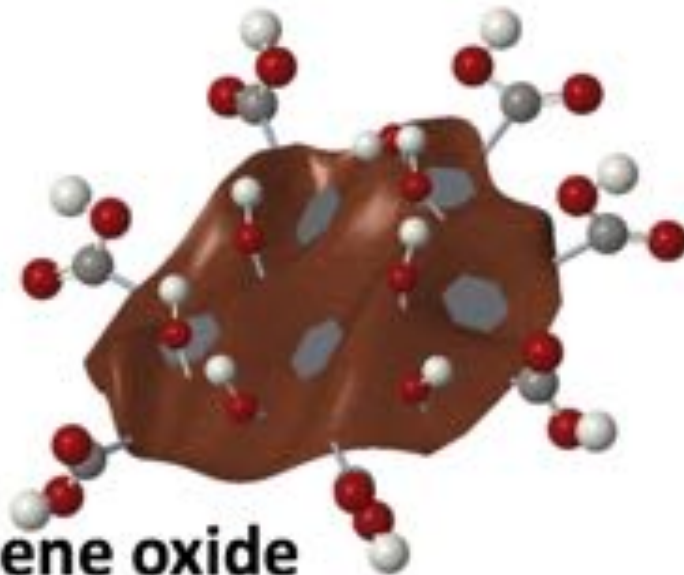
Esther García-Talavera,^{1,2,3,4,5,6} Eva Vellido,² José María Vázquez,² Alfonso J. Gil,² María Lema,² and Eduardo Rey²

Clay vs. Graphene oxide (GO)

Clay



'House-of-cards'



GO

Graphene oxide

2D

Amphiphile

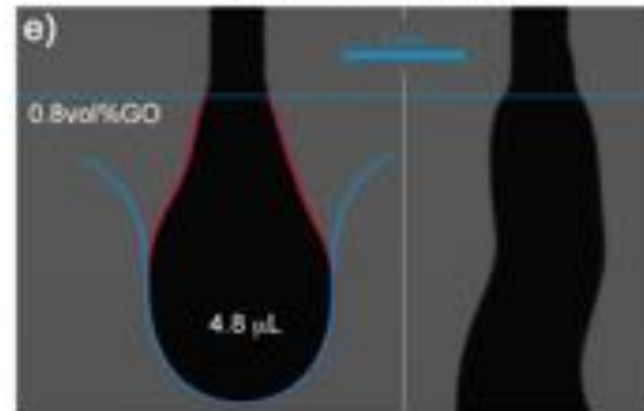
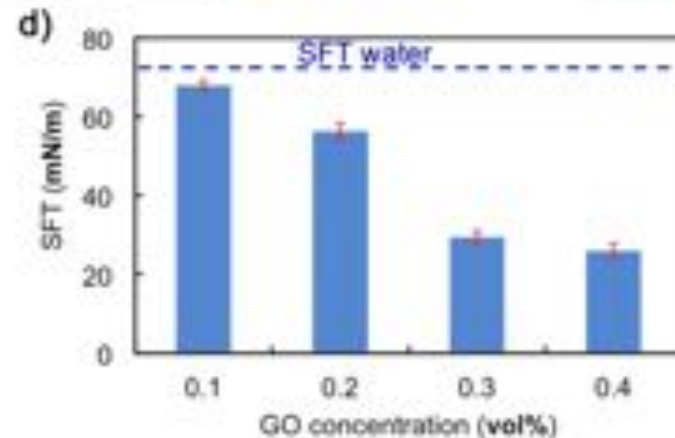
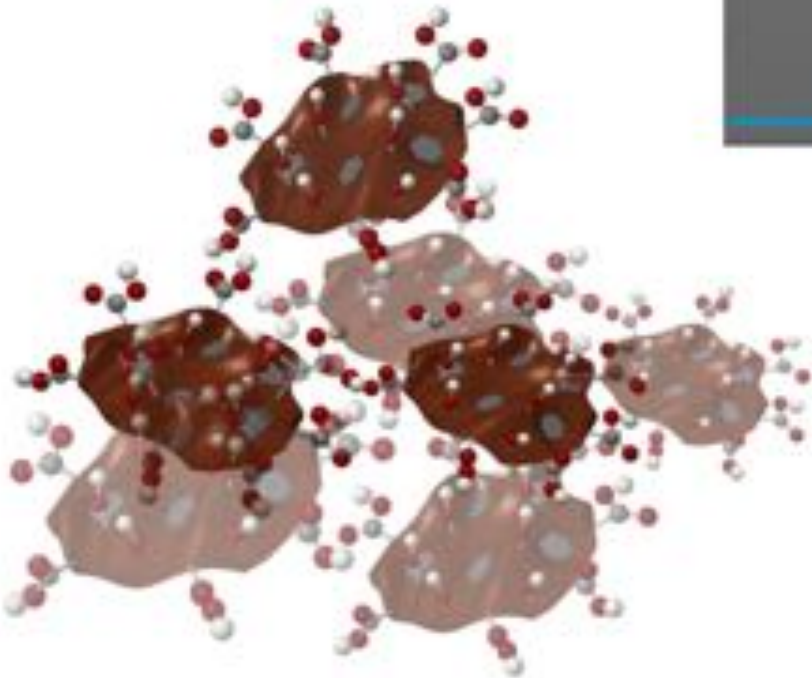
Multiple functionalities

Interactions across flakes

Flexible (can twist and bend)

MULTIPLE ROLES AS AN ADDITIVE

Surface tension – pendant drop



© 2004 Blackwell Publishing Ltd, *Journal of Internal Medicine* 255: 109–116

3D printing with 2D colloids: designing rheology protocols to predict 'printability' of soft-materials

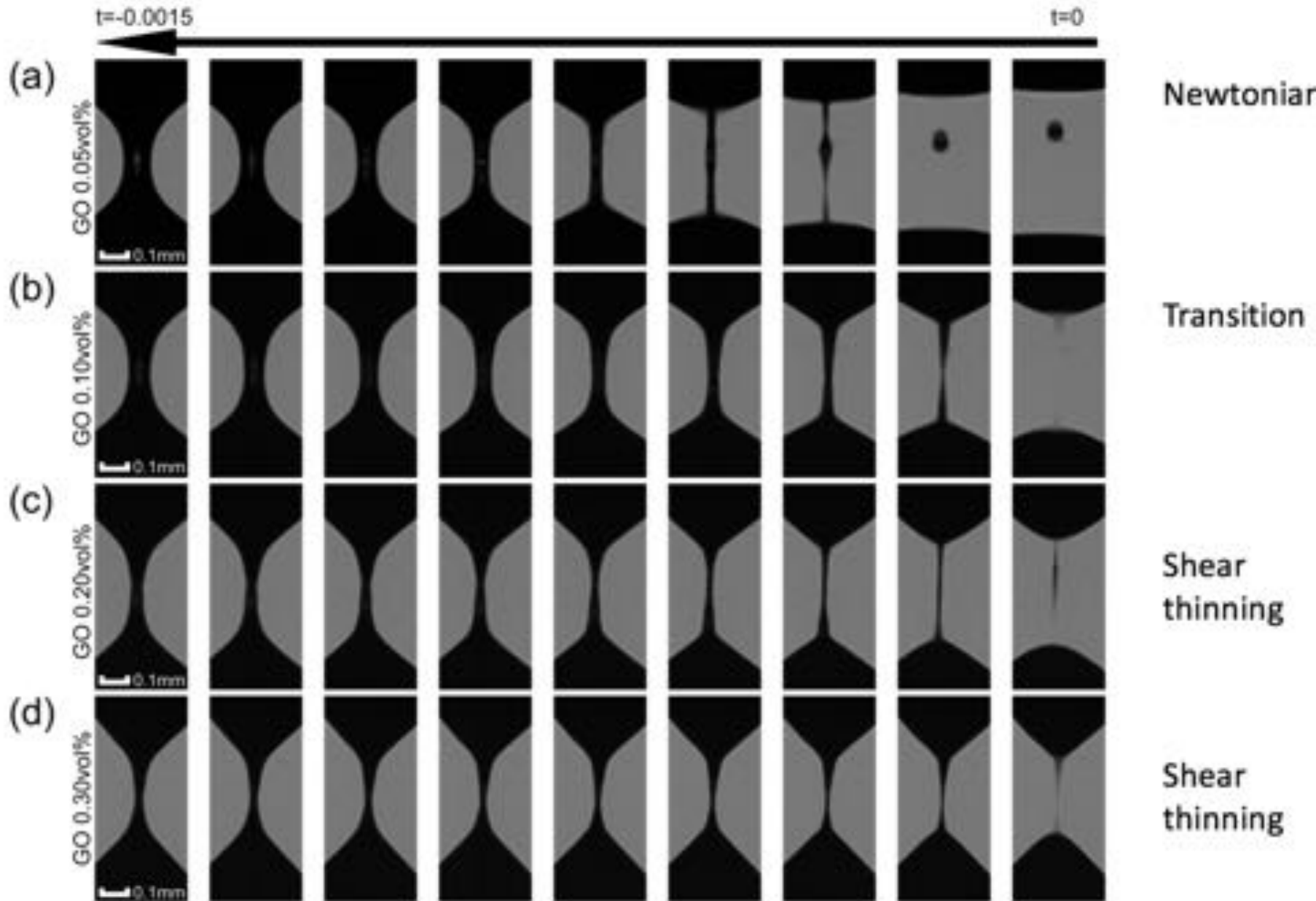
[illegible]

© 2004 Blackwell Publishing Ltd, *Journal of Internal Medicine* 255: 105–112

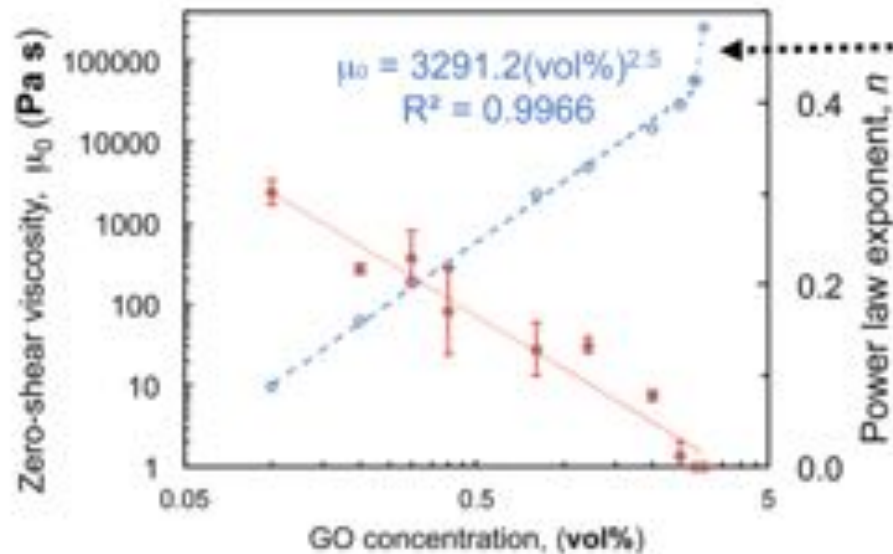
Copyright © 2004 John Wiley & Sons, Inc. All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as may be permitted in writing by John Wiley & Sons, Inc. This publication is registered at the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923.

Received 29 September 2008; Accepted 10 November 2008

Extensional rheology of GO networks



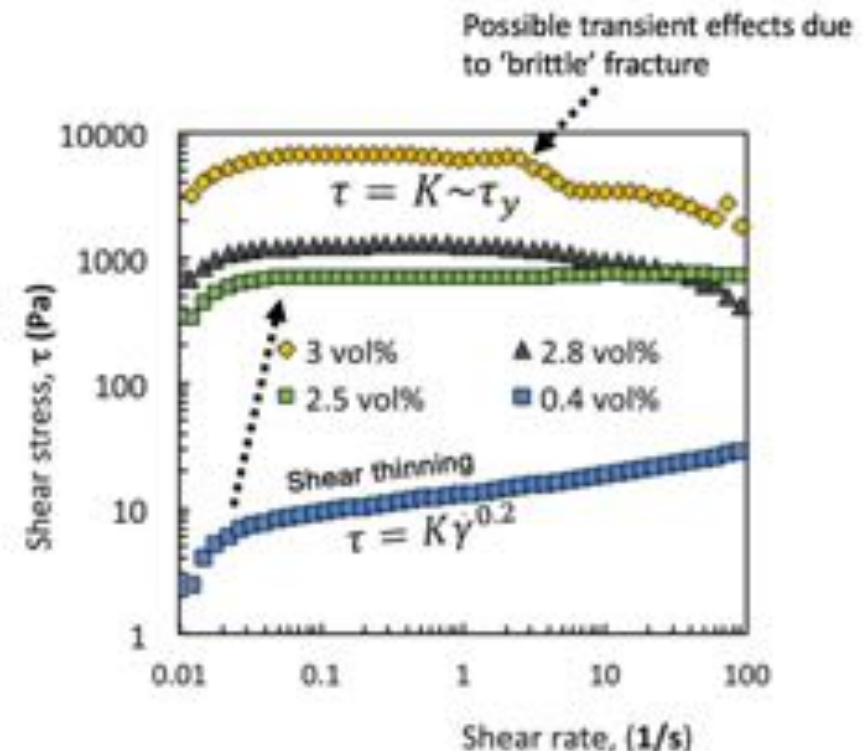
Shear rheology of GO networks



At concentrations of 3 vol% GO μ_0 increases up to values in the order of 250 kPa and does not follow the same power-law exponent.

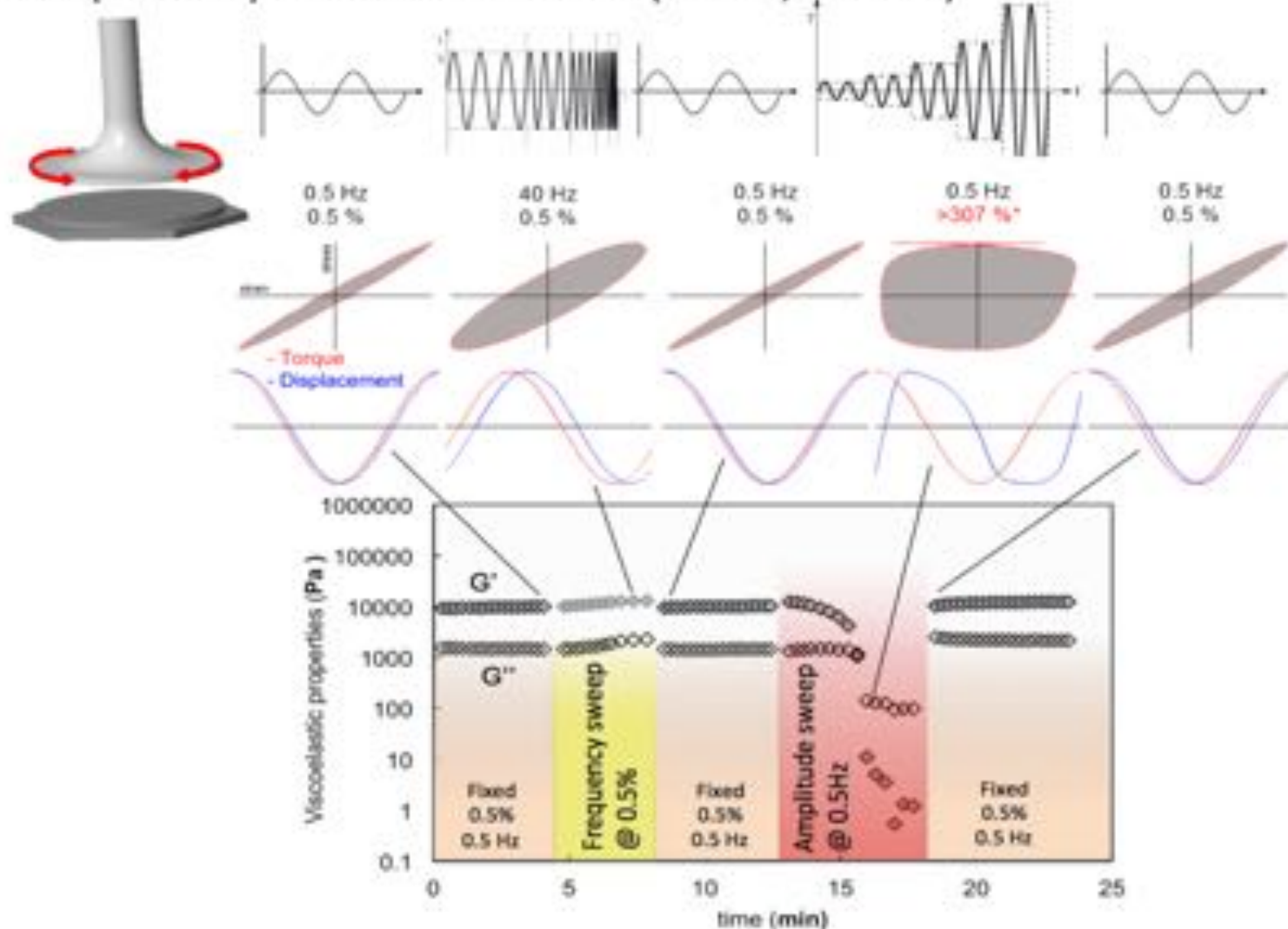
At 'printable' concentrations (2.5-3 vol%) the stress becomes essentially independent of the shear rate.

Transition from a power law behaviour ($\tau \sim K\dot{\gamma}^n$) to a regime where the stress is constant ($\tau = K \sim \tau_y$).



Oscillatory rheology of GO networks

Example: 5-steps 'structure' evolution (TA HR1, ARES G2)

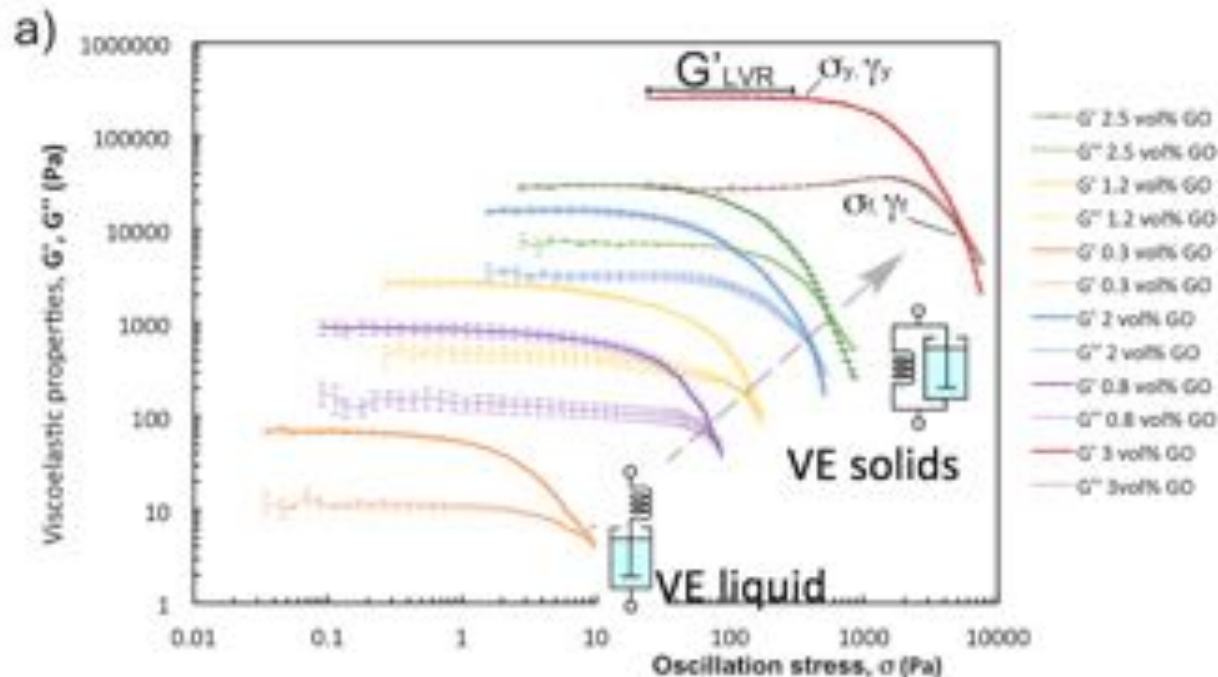
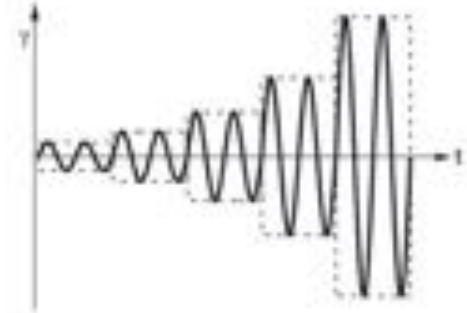




Quantifying printability: break down and flow



From an amplitude sweep: we determine the @rest structure (G'_{LVR}) 'yield and flow stress values' σ_y and σ_f to quantify the internal structure.



Flow transition index

$$FTI = \sigma_f / \sigma_y$$

Low FTI values
'brittle' soft material

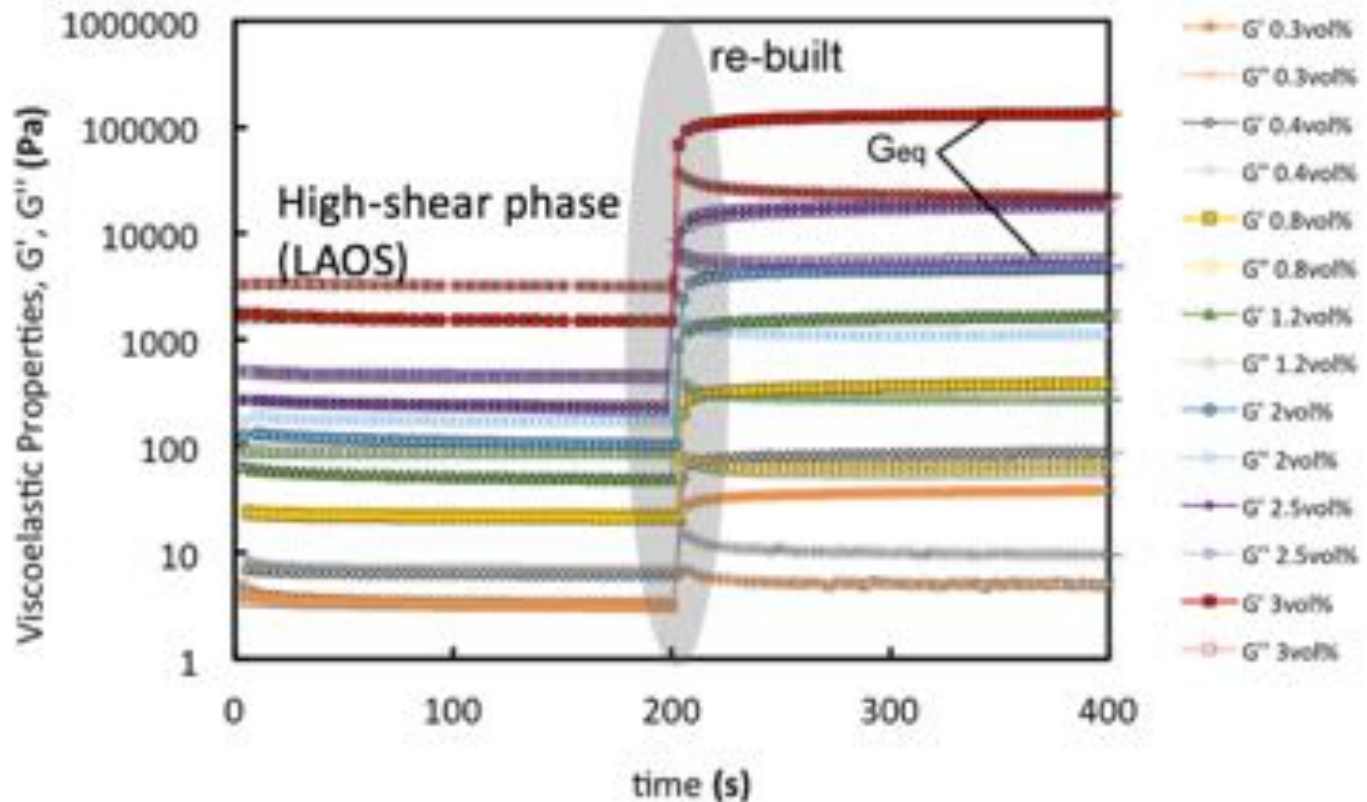
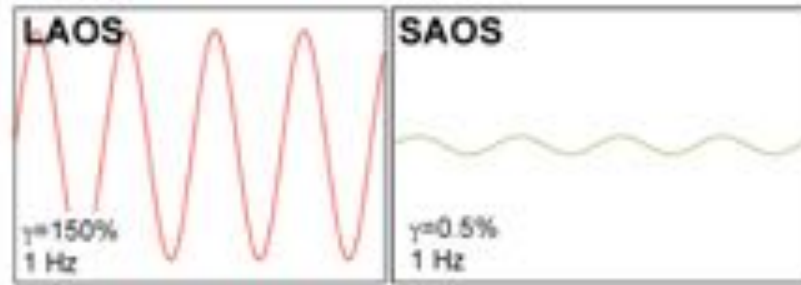


Quantifying printability: rebuild

Recovery tests

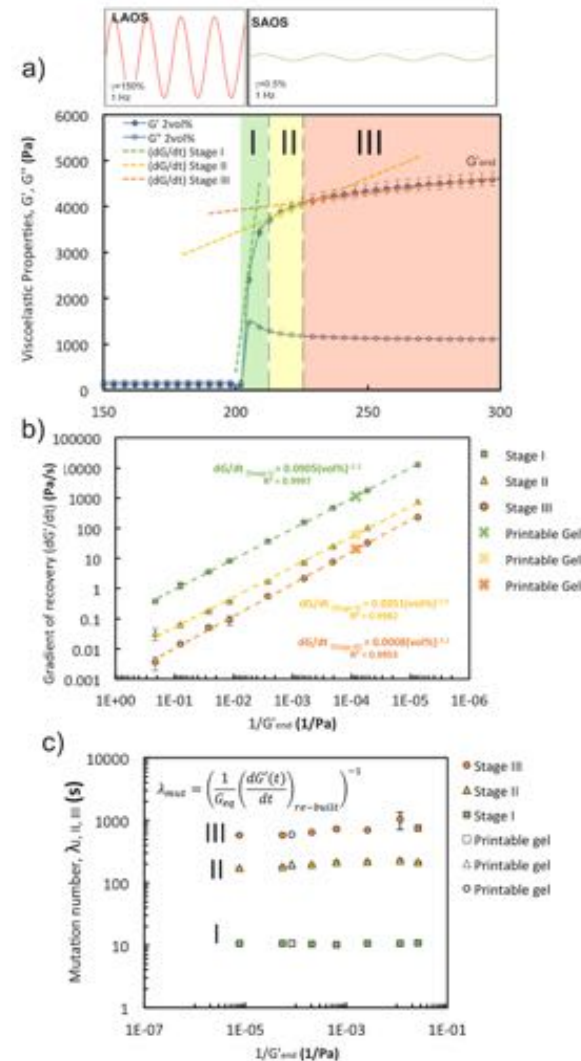


a)





Quantifying printability: rebuild

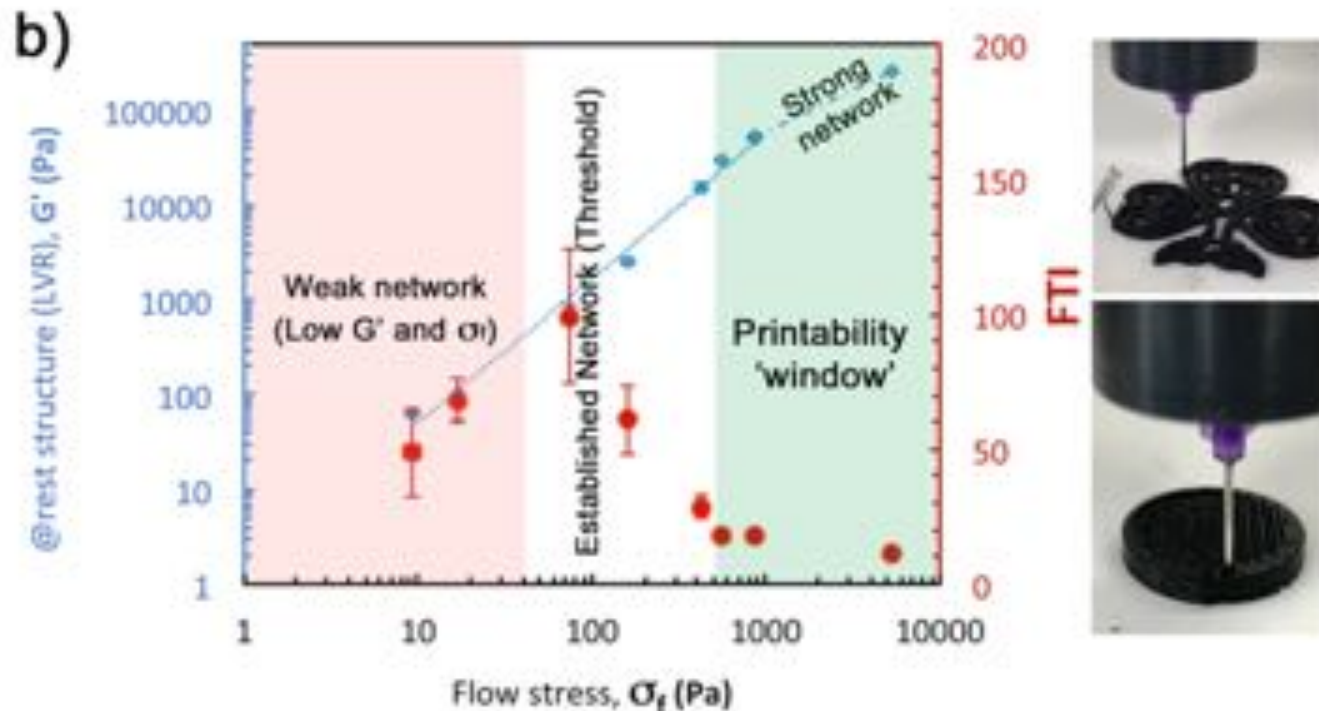
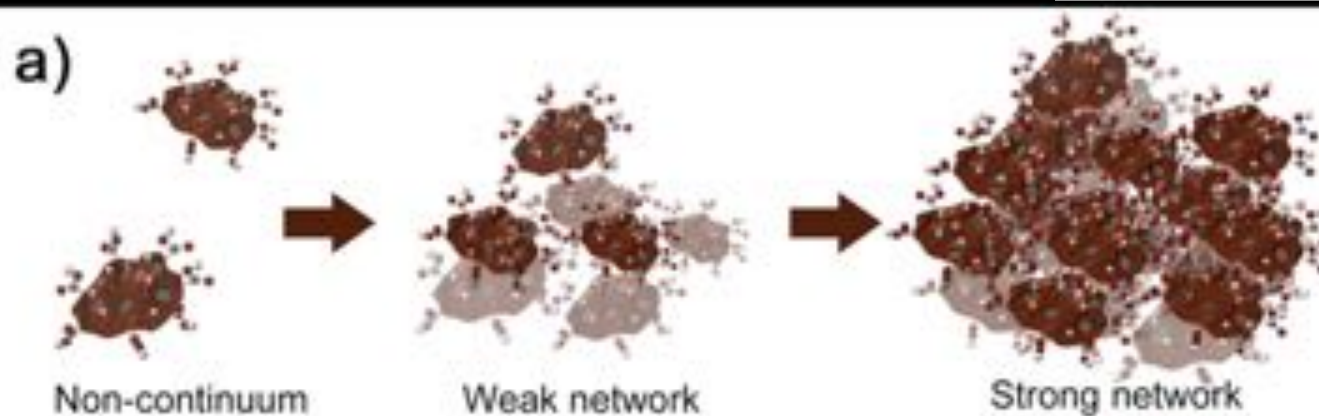


The recovery kinetics scales with G' !

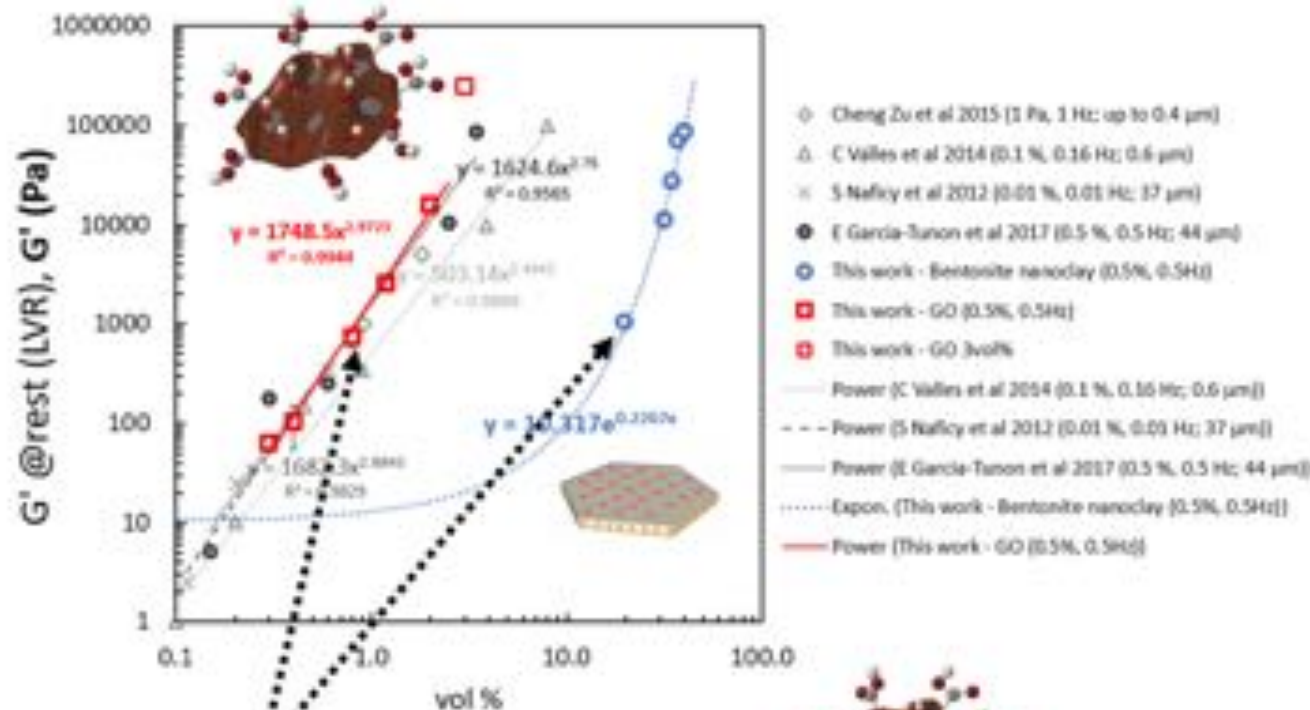


'Printability' of GO networks

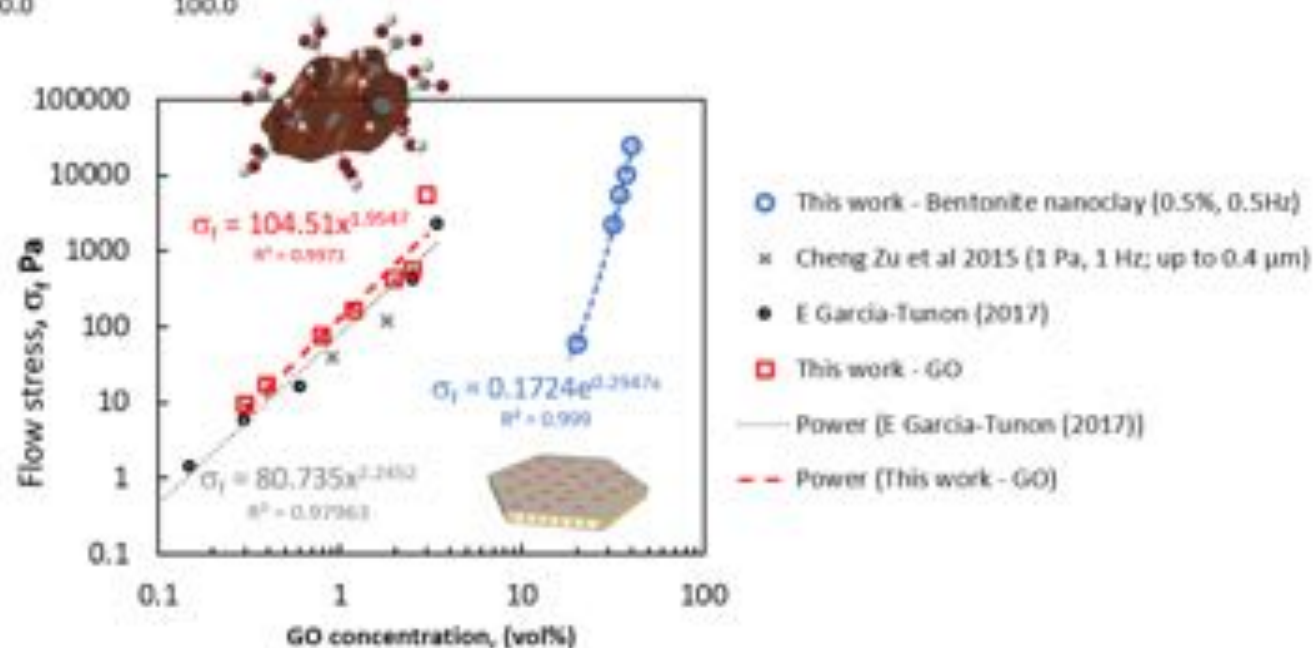
[No Title]



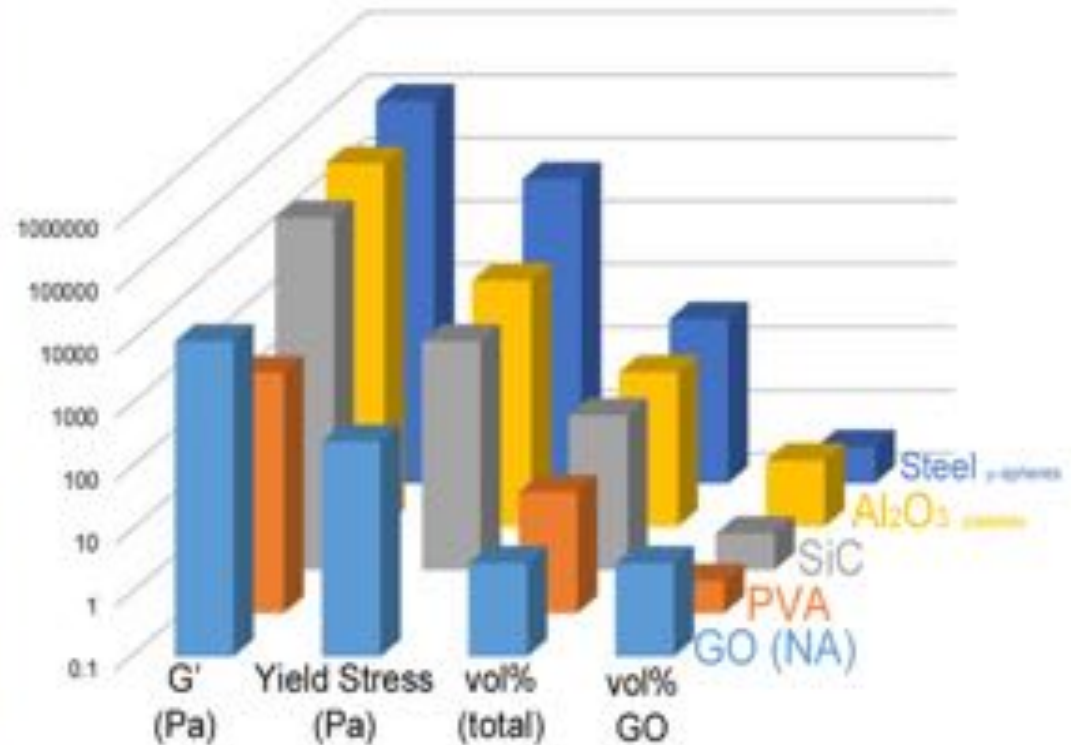
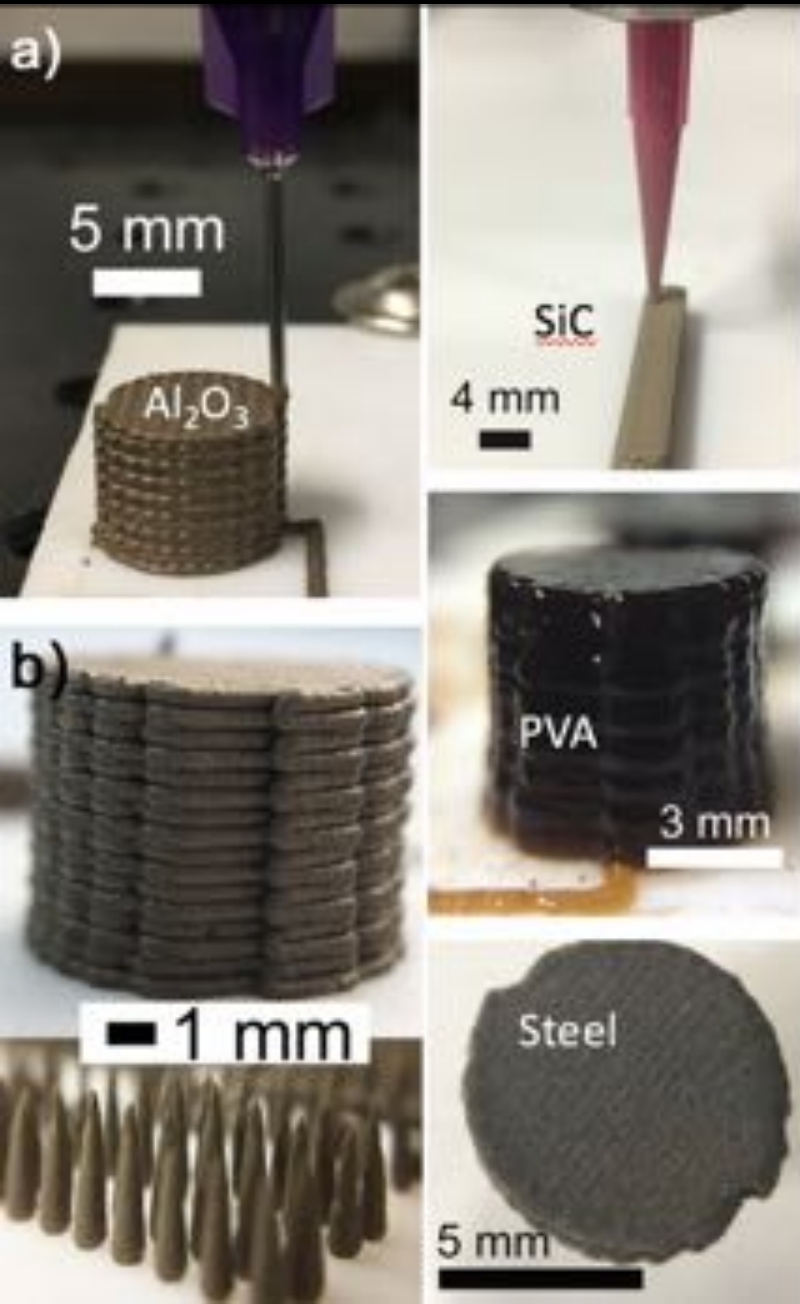
2D Colloids of Graphene oxide (GO) vs nanoclay



We need 10 times more nanoclay than GO to achieve G' and σ_f values in the same order of magnitude.



GO – multifunctional additive



APPLIED MATERIALS
INTERFACES

www.applied.org

Graphene Oxide: An All-in-One Processing Additive for 3D Printing

Esther García-Tuñín,^{1,2,3,4,5} Eran Feldman,¹ Han Zheng,¹ Eleonora D'Alagni,¹ Alan Leong,¹ and Eduardo Saiz¹

¹Center for Advanced Resin-based Composites, Department of Materials, Imperial College London, Royal School of Mines, 270a
Cannon Road, South Kensington, London SW7 2BX, U.K.

²Materials Innovation Factory & School of Engineering, University of Liverpool, Hartree Hughes Building, Newcastle 168, Liverpool
L69 3GH, U.K.

© Supporting Information

Library of water-based formulations with tuned rheology to aid the printing of advanced materials (*high added value 3D printing*).

pH-responsive

Poster: 'Tuning the rheology of hydrophobic materials in aqueous systems using responsive surfactants' **Emma Jones**



Thermo-responsive
gels

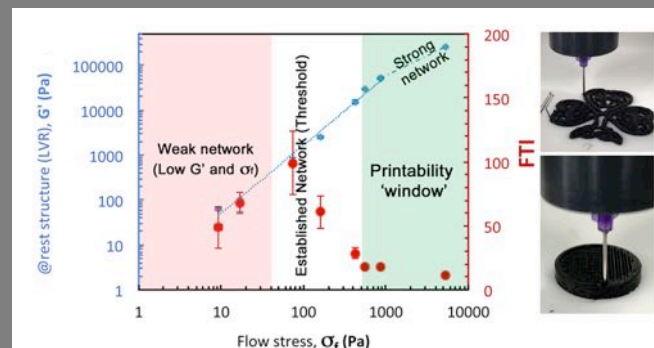


2D colloids

Poster: 'Formulation and 3D printing of carbon-based conductive inks for energy storage devices' **Andrew Corker**

Rheology protocol to quantify 'printability' of GO suspensions based on three rheology parameters:

@rest structure or network stiffness (G'_{LVR}),
flow stress, σ_f (when $G' = G''$),
and flow transition index FTI (σ_f / σ_y).





PhD Students

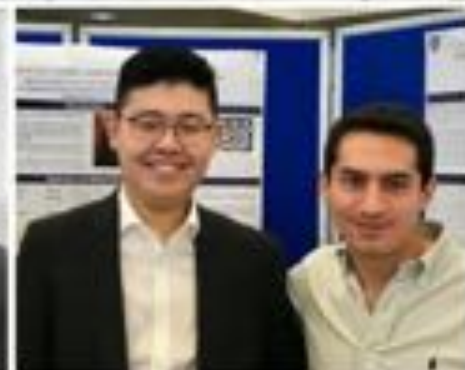
Andrew Corker
Emma Jones
Alice Brettle

MSc students

Alfred Cruz Davila
Yang Lyu

UG Mech Eng Students

Elimear McArteer
Jack Bentley
Jonathan Colville



Acknowledgements

Prof E Saiz, CASC, Imperial College London
(EPSRC grant 'Graphene 3D Networks')



Engineering and Physical Sciences
Research Council



The Leverhulme Trust



The Leverhulme Research Centre
for Functional Materials Design

Fundación Barrié