FEMS

EUROMAT2013

European Congress and Exhibition on Advanced Materials and Processes

SEVILLA 8 - 13 September **2013**

SPM socie mat sociedad española de materiales

Final Program

EURO MAT 2013 | HOTEL **BARCELÓ RENACIMIENTO**

http://www.euromat2013.fems.eu

TUESDAY 10 SEPTEMBER 2013 / AM2				
Symposium	D2I	D2II	D3II	E1III
Room	Sevilla 1	Andalucía 1	Cartuja	España 2
Session Title	Nanoindentation I	In-situ Micro- and Nano-Mechanical Characterisation I	Multiscale and Thermodynamics Modeling - from Atomic-Scale Properties to Macroscopic Behavior IV	Fuel Cell Electrodes II
Chairperson	T. Chudoba			G. Gebel
11:00	*ORAL* AN APPRAISAL OF CURRENT METHODOLOGIES FOR THE STUDY OF CREEP DURING INDENTATION **James Dean** (University of Cambridge) Bill Clyne	*HIGHLIGHT* SLIP MECHANISMS IN BCC SINGLE CRYSTALS: IN-SITU LAUE DIFFRACTION **Helena Van Swygenhoven** (Paul Scherrer Institut) Cecile Marichal, Steven Van Petegem, Camelia Borca	*INVITED / KEYNOTE* POLYMER NETWORK SIMULATIONS AT MESOSCOPIC LEVEL **Georgios Vogiatzis** (National Technical University of Athens) Grigorios Megariotis, Christos Tzoumanekas, Doros Theodorou	*INVITED / KEYNOTE* THIN FILMS OF MIXED IONIC-ELECTRONIC CONDUCTING MATERIALS FOR SOLID OXIDE FUEL CELLS **Jose Santiso** (Research Centre for Nanoscience and Nanotechnology, ICN-CSIC) Jaume Roqueta, Roberto Moreno, James Zapata, Mónica Burriel, Andrea Cavallaro, John Kilner
11:20	*ORAL* NANOINDENTATION CREEP TESTING OF FCC METALS AT ELEVATED TEMPERATURES **Gaurav Mohanty** (EMPA - Swiss Federal Laboratories for Materials Science and Technology) Krishna Rajan, Johann Michler	*ORAL* TEMPERATURE DEPENDENT SIZE EFFECTS IN LIF [111] SINGLE CRYSTALS **Rafael Soler Arnedo** (IMDEA Materials Institute) Jeffrey Wheeler, Jon Mikel Molina-Aldareguía, Chang Hyung-Jun, Javier Segurado, Johann Michler, Javier Llorca		
11:40	*ORAL* INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF POLYMERIC MATERIALS WITH THE INSTRUMENTED INDENTATION TEST **Bernd Binder** (Helmut Fischer GmbH Institut Für Elektronik Und Messtechnik) Tanja Haas	*ORAL* INFLUENCE OF DISLOCATION PILE-UPS ON MECHANICAL PROPERTIES OF MICROCANTILEVERS: NEW INSIGHTS VIA IN SITU MULAUE AND IN SITU SEM BENDING EXPERIMENTS. **Marlene Kapp** (Erich Schmid Institute of Materials Science, Austrian Academy of Science, Leoben, Austria) Christoph Kirchlechner, Reinhard Pippan, Jean-Sébastien Micha, Olivier Ulrich, Gerhard de hm	*ORAL* MULTISCALE MODELING OF COMPOSITE STRUCTURE-PROPERTY RELATIONS: APPLICATION TO ELECTRON TRANSPORT IN CARBON NANOTUBE REINFORCED POLYMER NANOCOMPOSITES. **Sergey Pyrlin** (Group of Computational and Theoretical Physics, Center of Physics and Department of Physics, University of Minho, Campus de Gualtar,Braga, Portugal) Marta Ramos	*ORAL* INTERACTION BETWEEN IRON-LIGAND COMPLEXES AND METAL ORGANIC FRAMEWORKS ON THE FUEL CELL PERFORMANCE OF NON-NOBLE METAL CATALYSTS **Adina Morozan** (Institut Charles Gerhardt de Montpellier, UMR 5253 CNRS - Université Montpellier II, Agrégats, Interfaces Et Matériaux Pour L'Energie) Juan Tian, Moulay Tahar Sougrati, Michel Lefèvre, Jean-Pol Dodelet, de borah Jones, Frédéric Jaouen
12:00	*ORAL* NANOINDENTATION AT ELEVATED TEMPERATURES: DESIGN AND EXPERIMENTS WITH NEW NANOINDENTATION DEVICE **Jiri Nohava** (CSM Instruments) Gaurav Mohanty, Jeffrey Wheeler, Johann Michler, Philippe Kempé	*ORAL* EX-SITU AND IN-SITU STUDY OF THE PLASTIC DEFORMATION OF INSB MICROPILLARS UNDER COHERENT X-RAYS **Ludovic Thilly (**niversity of Poitiers**)** Vincent Jacques, Dina Carbone, Rudy Ghisleni, Christoph Kirchlechner	*ORAL* EFFECT OF INTERFACES ON THE MELTING OF PEO CONFINED IN TRIBLOCK PS-B-PEO-B-PS COPOLYMERS **Emmanuel Beaudoin** (Université Paris-Sud 11) Michael Robinet, Trang Phan, Renaud Denoyel, Patrick Davidson, Denis Bertin, Renaud Bouchet	*ORAL* LA2-XSRXCOO4-D CATHODE MATERIALS FOR FUEL CELLS: TRANSPORT, DIFFUSION AND EXCHANGE PROPERTIES **Guilhem Dezanneau** (Lab. SPMS, Ecole Centrale Paris) Yang Hu, Vincent Thoréton, Alistar Ottochian, Caroline Pirovano, Rose-Noelle Vannier
12:20	*ORAL* MECHANICAL TESTING OF THIN FILMS UP TO 1000 °C **Daniel Leisen** (Karlsruhe Institute of Technology) Manuel Dany, Radoslav Rusanov, Oleg Jakovlev, Tino Fuchs, Chris Eberl, Heinz Riesch-Oppermann, Oliver Kraft	*ORAL* MEASURING STRAIN AND DEFECTS IN INDIVIDUAL MICROCRYSTALS: SYNCHROTRON MICRODIFFRACTION TECHNIQUES COMBINED WITH IN SITU LOADING **Simon Langlais** (SIMaP-Grenoble INP) Marc Verdier, Guillaume Beutier, Bruno Gilles, Maxime Dupraz	*ORAL* MODELING CONSTITUTIVE AND MICRO-SCALE FRICTIONAL BEHAVIOR OF PTFE **Mads Sonne** (Technical University of de nmark) Jesper Nørregaard, Jesper Hattel	*ORAL* DEVELOPMENT AND CHARACTERIZATION OF PTNI/PTNISN ALLOYS FOR APPLICATION AS CATALYSTS FOR DIRECT ETHANOL FUEL CELLS **Deyse Carpenter** (University of Blumenau) Vilson Fusiger
12:40	*ORAL* MEASUREMENT OF THE YOUNG MODULUS AT WARM TEMPERATURE **Michel Darrieulat** (Ecole des Mines de Saint-Etienne) Asdin Aoufi, Christophe Desrayaud	*ORAL* IN-SITU INDENTATION IN THE TRANSMISSION ELECTRON MICROSCOPE OF A DUAL PHASE MG ALLOY REINFORCED WITH GAMMA-MG17AL12 **Harshal Mathur** (Institute of General Materials Properties (WW1), Department of Materials Science and Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany) Mirza Mackovic, Souad Benrhaiem, Dorothea Amberger, Patricia Donnadieu, Erdmann Spiecker, Sandra Korte	EMPTY SLOT	*ORAL* EFFECT OF THE DOPANT AMOUNT ON THERMAL ANALYSIS AND ELECTRICAL PROPERTIES OF SR1-XLAXTIO3±D AND SR1-(3X/2)LAXTIO3±D (X=0,0.1,0.2,1/3 AND 0.4) SYSTEMS AS ANO DE MATERIALS FOR SOFCS. **María Gálvez Sánchez** (Universidad de Castilla-La Mancha. Instituto de Investigación de Energías Renovables) Juan Carlos Ruiz Morales, Juan Carlos Pérez Flores, Flaviano García Alvarado, Jesús Canales Vázquez

Multiscale modeling of composite structure-property relations: application to electron transport in carbon nanotube reinforced polymer nanocomposites.

Sergey V. Pyrlin[1,2,3]; Marta M.D. Ramos [1]

1. Group of Computational and Theoretical Physics, Center of Physics and Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal;
2. I3N - Institute for Nanostructures, Nanomodelling and Nanofabrication, IPC - Institute for Polymers and Composites, University of Minho, Campus de Azurem, 4800-058 Guimaraes, Portugal;
3. Department of Physics, Bauman Moscow State Technical University, 2nd Bauman street. 5, 105005 Moscow, Russia;

pyrlinsv@fisica.uminho.pt

Development of functional composite materials by addition of inorganic inclusions to polymer matrix attracts growing attention in last decades. However such material characteristics depend not only on the concentration and properties of nanoinclusions but also on their distribution inside embedding polymer, which complicates prediction and optimization of composite properties. Carbon nanotubes (CNT) attract particular interest as reinforcement material due to their unique properties tunable by doping and functionalization.

Different properties of carbon nanotubes were successfully studied *in silico* in numerous papers by atomistic calculations. However computational chemistry is limited to systems containing hundreds to several thousands of atoms so only fragments of polymer chains and nanotubes are accessible. Meanwhile optical microscopy analysis shows that industrial-scale CNT-polymer composites contain distribution irregularities and agglomerates of CNTs up to ~10 micron size [1].

Charge transport in such composites mostly explained by electron tunneling between conductive inclusions, probability of which depends on nanotube's electronic structure as well as on tunneling distance and local electric field in the contact region, affected by the presence of other conducting inclusions. To facilitate the investigation of CNT-polymer composites' electric properties a two-level modeling procedure is suggested: first, local density of states (LDOS) around CNT's Fermi level is evaluated from *ab initial* calculations including the effect of doping and functionalization, than a Monte Carlo simulation of charge transport between CNTs is carried out where the tunneling probability is estimated using previously calculated LDOS and simplified representation of electronic wave functions in the inter-CNT space as spherical or cylindrical waves.

The suggested procedure, although very simplistic, allows charge transport studies on a length scales of ~100 um compared to the scale of CNTs' distribution irregularities in composites and direct comparison with experimental data.

[1] G. Olowojoba, S. Sathyanarayana, B. Caglar, B. Kiss-Pataki, I. Mikonsaari, C. Hübner, and P. Elsner. *Polymer*, 54(1):188 – 198, 2013.

Symposium D3. II Multiscale modeling - from atomic-scale properties to macroscopic behaviour.

CONTACT

EUROMAT2013
Sevilla 8-13 Sept
Spain

Multiscale modeling of composite structure-property relations: application to electron transport in CNT reinforced polymer nanocomposites

Sergey V. Pyrlin [1,2,3]; Marta M.D. Ramos [1]*

1. *Group of Computational and Theoretical Physics, University of Minho, Portugal;* www.gfct.fisica.uminho.pt
2. *I3N - Institute for Nanostructures, Nanomodelling and Nanofabrication, Portugal;* www.i3n.org
3. *Bauman State Technical University, Russia;* www.bmstu.ru

**pyrlinsv@fisica.uminho.pt*

This project has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 238363

CONTACT

ITN "CONTACT": http://www.contactproject.eu/

The research aim of ITN "CONTACT" is the tailored industrial supply-chain development of CNT-filled polymer composites with improved mechanical and electrical properties

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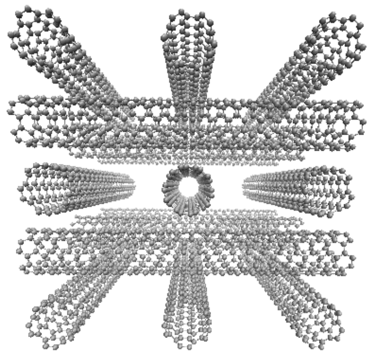
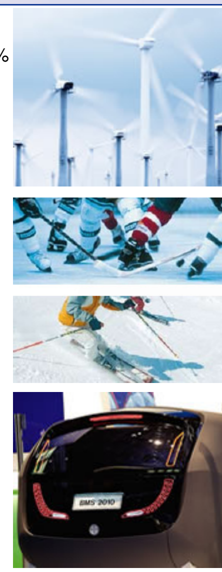
Applications of polymer-CNT composites:

Z. Spitalsky et al. Prog. in Polymer Sci. 2010, vol. 35, p. 357-401
Young modulus & Tensile strength increase ~***10x*** by adding 1 vol%
Conductivity increase ~***16* orders of magnitude**
Percolation threshold ~**0.003 wt%**





* Photographs from www.baytubes.com

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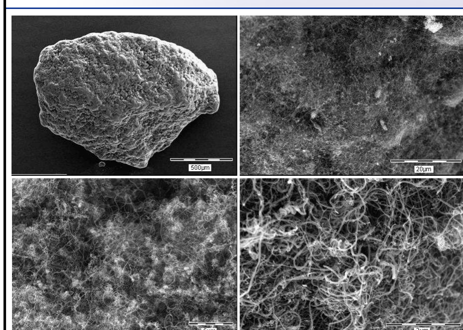
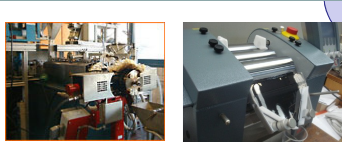
Industrial scale CNT production:

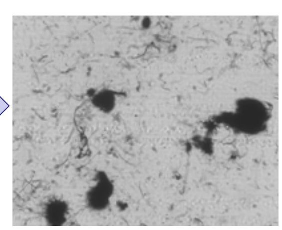


- I've made a composite with 2 w.% of nanotubes!

- Indeed… and looks like all of them are here.

* Micro photograph from www.baytubes.com





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CONTACT

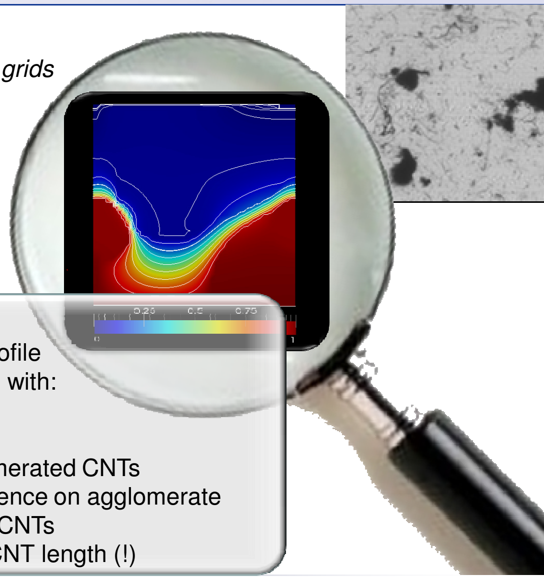
Motivation: *why multiscale?*

Continuum level:

SOR algorithm on finite grids

$$\nabla(\sigma\nabla U) = 0$$

$$\sigma = \sigma_0(v - v_p)^\alpha$$



Allows to investigate:
1. Voltage/Current profile
2. Resistivity variation with:
   - CNT content
   - agglomerate size
   - fraction of agglomerated CNTs

Predicts weak dependence on agglomerate size after 1.7-2 vol. % CNTs

Agglomerate size >> CNT length (!)

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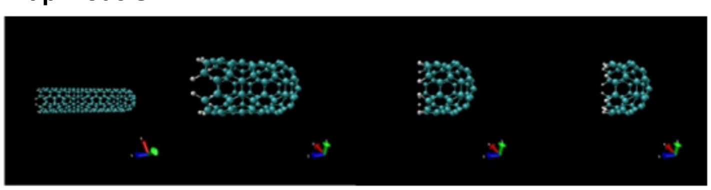
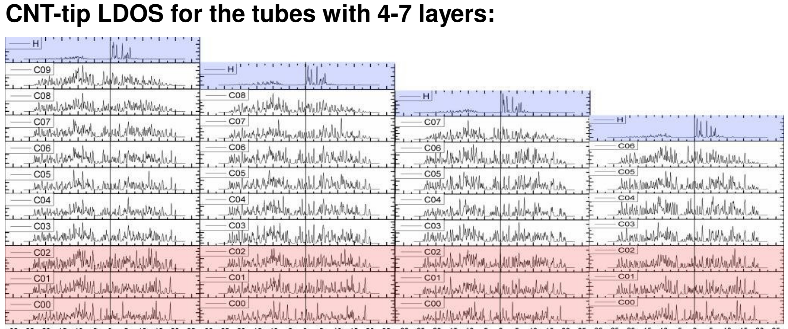
CONTACT

Motivation: *why multiscale?*

CNT-tip models:



CNT-tip LDOS for the tubes with 4-7 layers:



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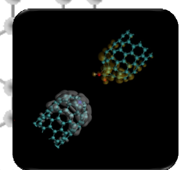
Imperial College London

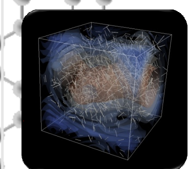
CONTACT

Multiscale picture:

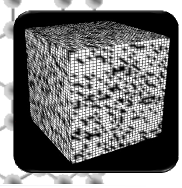
Atomistic level
- **Input:** atomic data, molecular geometry
- **Methods:** QC & MD
- **Results:** (modified)CNT properties – IP,EA, charge hopping probabilities etc.;



Mesoscopic level
- **Input:** composite morphology, external fields, matrix properties;
- **Methods:** MC, RRN;
- **Results:** composite FE properties;



Application: Continuum level
- **Input:** device design, material properties;
- **Methods:** FEM, analytical modeling etc.;
- **Results:** device properties;



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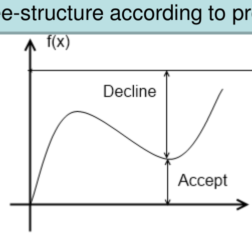
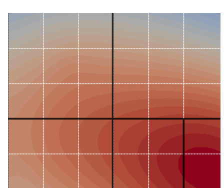
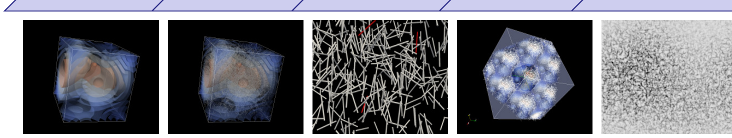
Generation procedure: acceptance rejection method

To achieve better parallel performance, space is divided into cells, arranged into tree-structure according to probability density





Predefined distribution density → "CNT web" following the distribution → Intersection correction → Periodic conditions → "Real-like" system for simulation & analysis



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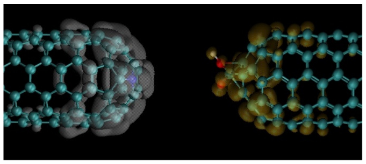
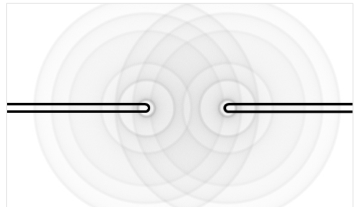
Electron tunneling simplified description:





$$W_{tot} = \frac{4\pi}{\hbar}\int_0^{eV} \rho_s(E_F - eV + \varepsilon)\rho_D(E_F + \varepsilon)|M|^2 d\varepsilon \quad M_{\varphi\psi} = \frac{\hbar}{2m}\int(\varphi^*\nabla\psi - \psi\nabla\varphi^*)dS$$

Tersoff – Hamann:*

$$\psi_n = \frac{A_n \exp(-k_n r)}{r} \quad k_n = \frac{\sqrt{2m|E_n|}}{\hbar} \Rightarrow M_{ij} = \frac{h}{2m}\frac{k_i k_j}{2\pi\hbar} e^{-(k_i+k_j)R}$$

Data required from atomistic level: **LDOS ρ(E)** in contact region

Resulting W_{tot} are used either as conductivity estimates (for RRN model) or tunneling probabilities (Monte Carlo charge propagation model)

** Theory of the scanning tunneling microscope*
J. Tersoff, D.R. Hamann, PRB 1985 Vol. 31(2) 805-813;

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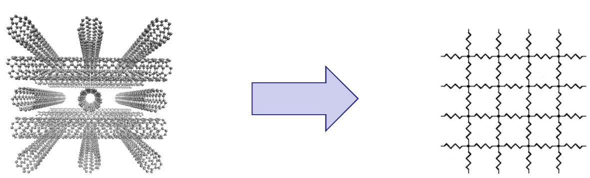
CONTACT

Random resistor network model:



$$\begin{cases} \sum_i I_{ij} = 0 \\ I_{ij} = \frac{V_i - V_j}{R_{ij}} \end{cases} \rightarrow V_i \sum_{j=2}^{n+2} a_{ij} = \sum_{j=2}^{n+2} a_{ij}V_j + a_{i1}V_1 + a_{i0}V_0 \xrightarrow{V_0=0, V_1=1} (\boldsymbol{I} - \boldsymbol{A})\boldsymbol{V} = \boldsymbol{B}$$

$$\boldsymbol{A} = \left[\frac{a_{ij}}{\sum_{j=2}^{n+2} a_{ij}}\right], \boldsymbol{B} = \left[\frac{a_{i1}}{\sum_{j=2}^{n+2} a_{ij}}\right]$$

Easy to implement;
Can model electric current dependence on morphology;
Misses charges interaction;

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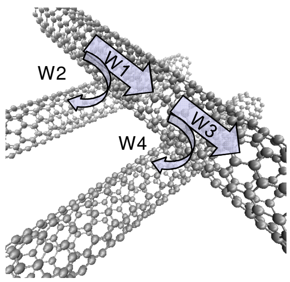
Monte Carlo simulation of charge propagation:



Current inside CNT ~mA;
Current in tunneling junctions ~ nA;
Ratio of effective time of *inter*- & *intra*tube transport:

$$t_{tun}/t_{CNT} \sim 10^5$$

Mesoscopic Simulation:
Monte Carlo simulation of charge transport between CNTs under effect of:

$$\vec{E}_{loc}(\vec{r}) = \vec{E}_{ext}(\vec{r}) + \vec{E}_e(\vec{r}) + \vec{E}_T(\vec{r}) + \vec{E}_{pol}(\vec{r})$$

Field of free charges: $\vec{E}_e(\vec{r}) = \sum \frac{e}{r_{ij}}$

Polarization field: $\vec{E}_{pol}(\vec{r}) = \sum \vec{E}_i^{dipole} = \sum \frac{3(\vec{p}_{Tpol}\vec{r}_{ij}) - r_{ij}^2\vec{p}_{Tpol}}{r_{ij}^5}$ $\quad \vec{p}_{pol} = \alpha_{ij}\vec{E}$

Thermal voltage fluctuations in contact region $f(V_T) = A_T exp\left(-\frac{cV_T^2}{2k_BT}\right)$

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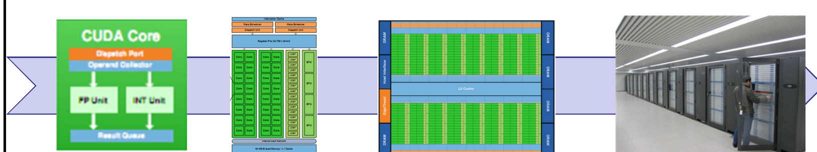
SEVENTH FRAMEWORK PROGRAMME

i3N Imperial College London

CONTACT

Realization:

NVIDIA CUDA Technology:



Rates of filling 168 um cube with 4um x 10 nm cylindrical inclusions:

Uniform distribution			Non uniform distribution		
0.5 vol. %	$18*10^6$ inclusions	5 min	0.5 vol. %	$18*10^6$ inclusions	9,2 min
1.0 vol. %	$35*10^6$ inclusions	33,5 min	1.0 vol. %	$35*10^6$ inclusions	155 min

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SEVENTH FRAMEWORK PROGRAMME

i3N

CONTACT Application: PC composites conductivity

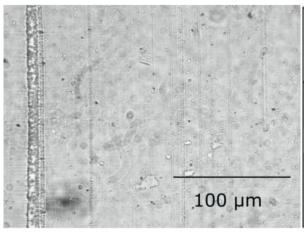


Jyri Tiusanen – sample preparation

Bernadeth Kiss-Pataki – microscopy

Anna Y. Matveeva – image analysis

Agglomerate size was determined from microscopy analysis of PC samples containing 3 vol. % of 1,5 um long CNTs.



Code	average agglomerate radius x_c, um	agglomerate radius dispersion w, um	Volume resistivity (ρv) average Ω.cm	stdev Ω.cm
F1	0.28	1.55	78,908	3,965
F2	0.40	1.47	6171,026	2205,548
F3	0.41	0.85	27,934	2,025
F4	0.10	0.66	46,451	6,973
F5	0.14	0.53	156,873	28,616
F6	0.10	0.76	23,274	4,244

Series of samples with close agglomerate parameters can exhibit **2 orders of magnitude difference** in resistivity.

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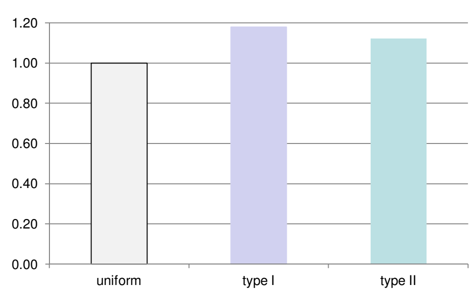
CONTACT Random Resistor Network analysis:

•**type 1:** x_c=0.4 um, w = 1.47 um, total agglomerate volume fraction 0.32% (corresponding to F2 series);
•**type 2:** x_c=0.1 um, w = 0.66 um, total agglomerate volume 1.1% (corresponding to F4 series);

Code	Volume resistivity (ρv) average Ω.cm	stdev Ω.cm
F1	78,908	3,965
F2	6171,026	2205,548
F3	27,934	2,025
F4	46,451	6,973
F5	156,873	28,616
F6	23,274	4,244



Conclusion: the 2 order of magnitude difference **cannot** be attributed solely to agglomerate size

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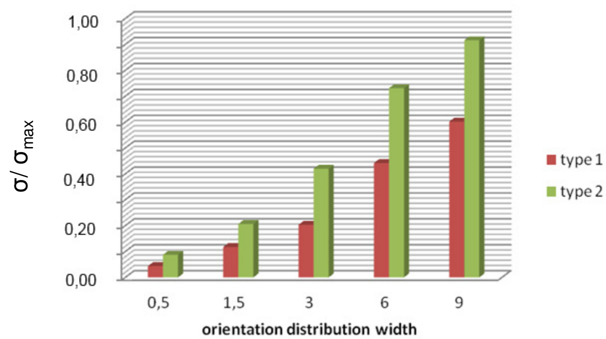
Random Resistor Network analysis:

Effect of CNT alignment on overall conductivity



Conclusion: the observed difference should be attributed to different degree of CNT alignment

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CONTACT

Work in progress:

<u>To be added soon:</u>

- Monte Carlo simulation of charge propagation
- various inclusion shapes (only spherically capped cylinders are implemented at the moment);

<u>Constant searching for:</u>

- Better intertube conduction models
- experimental data on alignment/wavness of CNT

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CONTACT

Acknowledgements:

1. The work is a part of the CONTACT project for the tailored supply-chain development of CNT-filled composites with improved mechanical and electrical properties funded by Marie Curie Initial Training Network "CONTACT" (FP7-PEOPLE-ITN-2008-238363) http://www.contactproject.eu/;
2. The Center of Physics of University of Minho research is sponsored by FEDER funds through the program COMPETE- Programa Operacional Factores de Competitividade and by national funds through FCT-Fundação para a Ciência e a Tecnologia, under the project PEst-C-FIS/UI607/2011-2012.

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THANK YOU!

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