



**Influence of Shear Flows and Long Chain  
Branching on the Rheological and Electrical  
Properties of Polypropylene/Carbon nanotube  
Composites**

Jixiang Li, Abderrahim Maazouz, Khalid Lamnawar\*

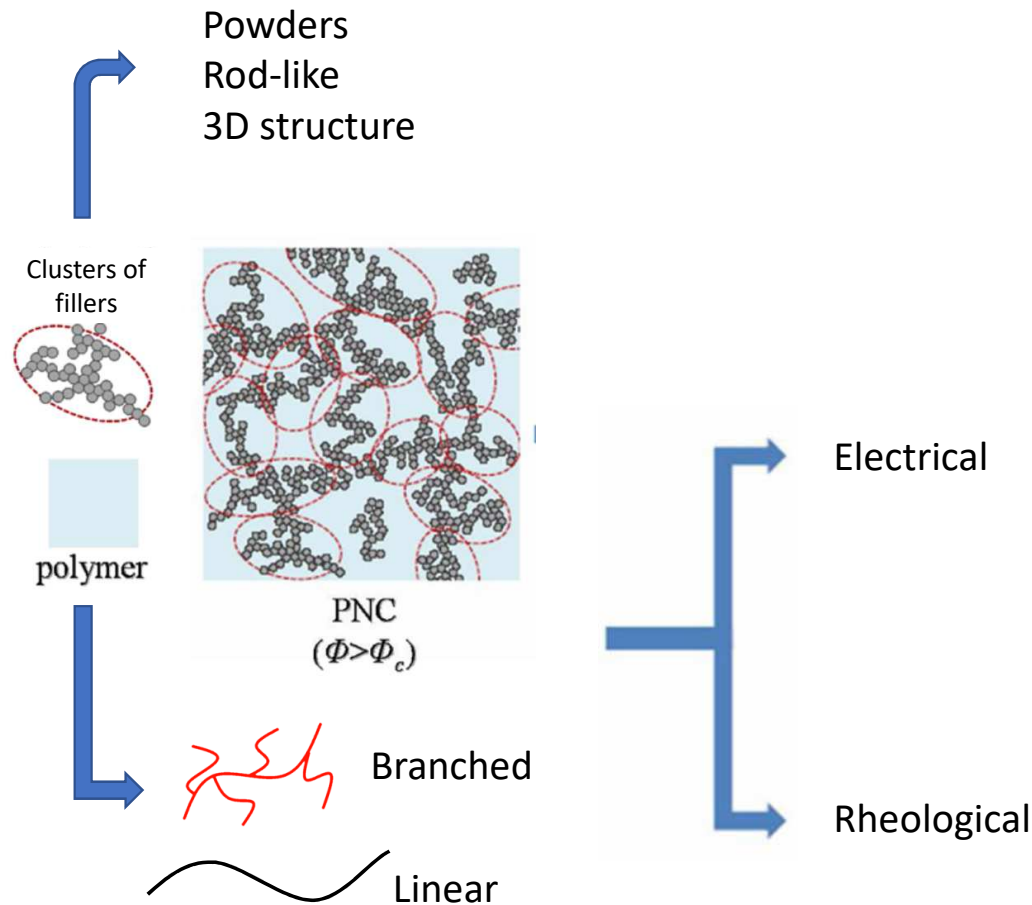
*\*Université de Lyon, CNRS, UMR 5223, Ingénierie des Matériaux  
Polymères, INSA Lyon, F-69621, Villeurbanne, France*

\* Auteur correspondant : [khalid.lamnawar@insa-lyon.fr](mailto:khalid.lamnawar@insa-lyon.fr)

**49<sup>èmes</sup> Journées  
d'Etudes des Polymères  
(JEPOs 2022)**

**Du 2 au 7 octobre 2022  
À Bussang (Vosges)**

# Background



Relationships between them???

# Background: Rheological Percolation

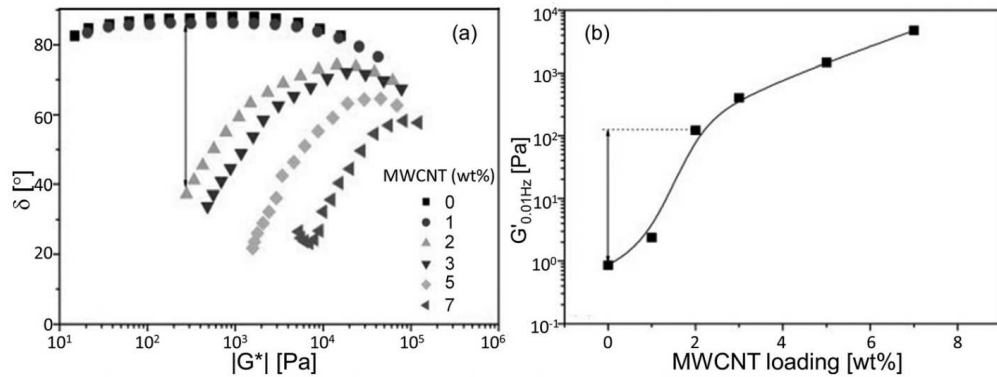


FIG. 1. (a) van Gurp–Palmen plot and (b)  $G'(\omega, \varphi)$  measured at 0.01 Hz as a function of MWCNT loading for PBT nanocomposite melts at 240 °C [Wu *et al.* (2007b)].

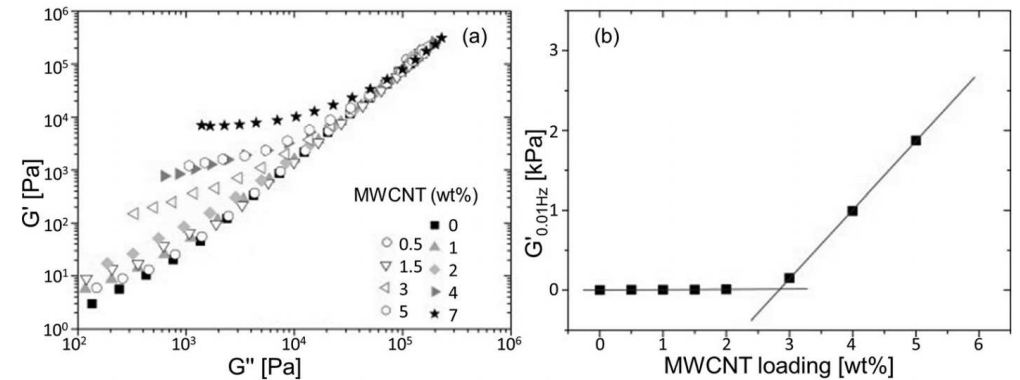


FIG. 3. (a) Han plots for carboxylic MWCNTs filled polylactide melts and (b)  $G'(\omega, \varphi)$  measured at 0.01 Hz as a function of MWCNT loading [Wu *et al.* (2008)].

[Yihu Song](#) and [Qiang Zheng](#), "Linear rheology of nanofilled polymers", *Journal of Rheology* 59, 155-191 (2015) <https://doi.org/10.1122/1.4903312>

# Background: Impacts to the percolation

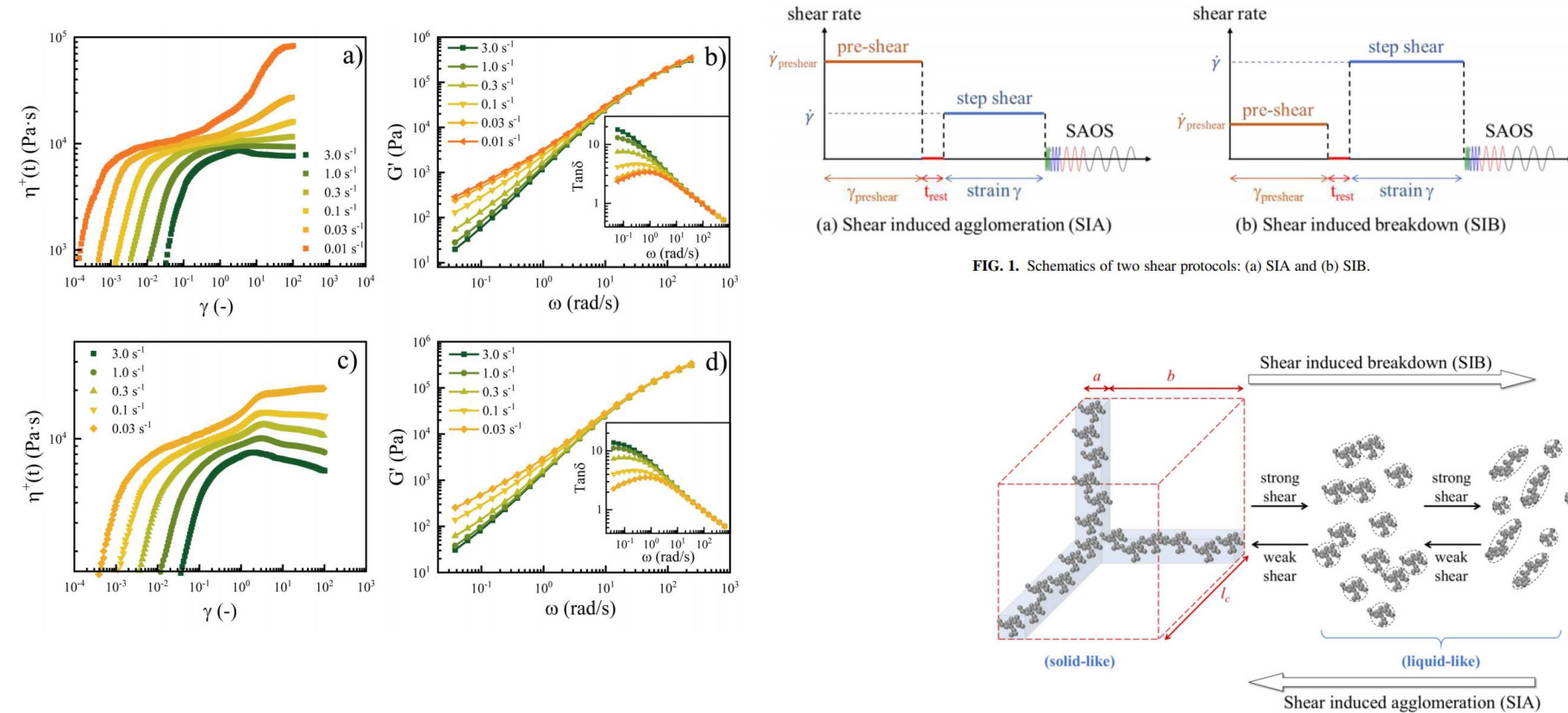


FIG. 1. Schematics of two shear protocols: (a) SIA and (b) SIB.

Benke Li, Ying Guo, Paul Steeman, Markus Bulters, and Wei Yu, "Shear-induced breakdown and agglomeration in nanoparticles filled polymer: The shift of phase boundary and kinetics", Journal of Rheology 65, 291-309 (2021) <https://doi.org/10.1122/8.0000032>

# Background: Impacts to the percolation

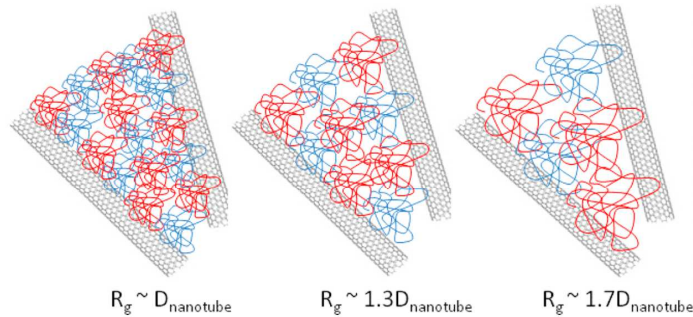
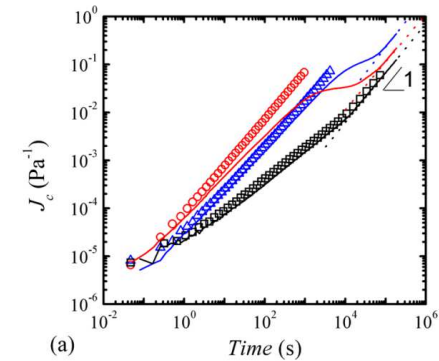


Figure 15. Scheme showing the possible differences in the interaction between macromolecules and CNTs as a function of molecular size (based on  $M_w$  values).

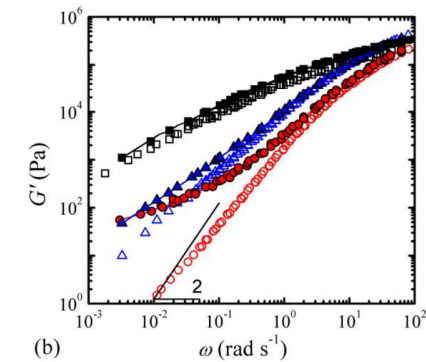
Table 1. Molecular and Melt Linear Viscoelastic Features ( $T = 140\text{ }^\circ\text{C}$ ) of the Neat Polyethylene Matrices and the Nanocomposites Studied<sup>a</sup>

sample	SCB CH <sub>3</sub> /1000C	$M_w$ kg mol <sup>-1</sup>	$M_w/M_n$	$M_z$ kg mol <sup>-1</sup>	$\eta_0$ (kPa s)		$J_e^0$ (mPa <sup>-1</sup> )	
					neat	CNT	neat	CNT
PE1	10.7	113	2.1	225	14.0	900	0.065	3.32
PE2	0	185	2.2	370	60.0	425	0.64	4.95
PE3	4.4	326	37.4	1990	1020	1460	2.30	2.96

<sup>a</sup>SCB: Short chain branching content.  $M_w$ : weight-average molecular weight  $M_z$ : z-average molecular weight.  $\eta_0$ : zero shear melt viscosity.  $J_e^0$ : linear steady-state recoverable compliance.



(a)

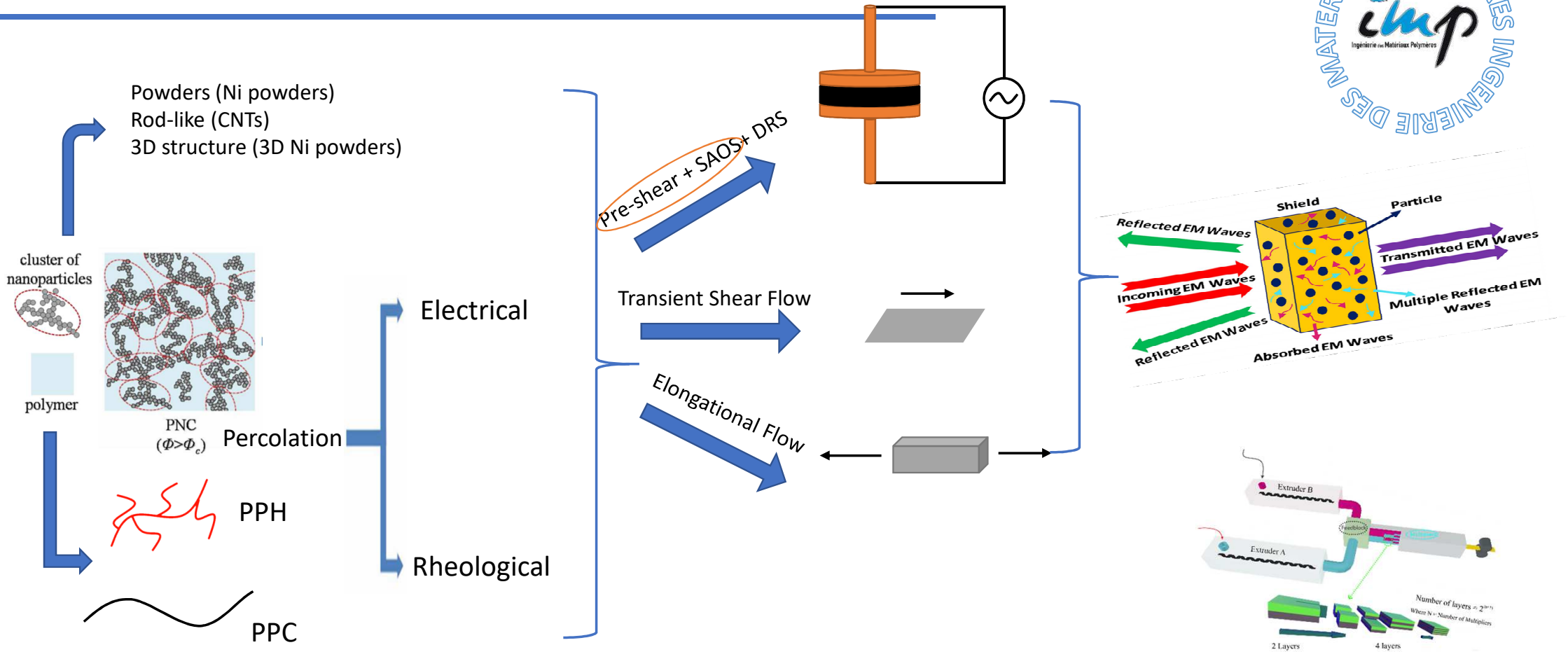


(b)

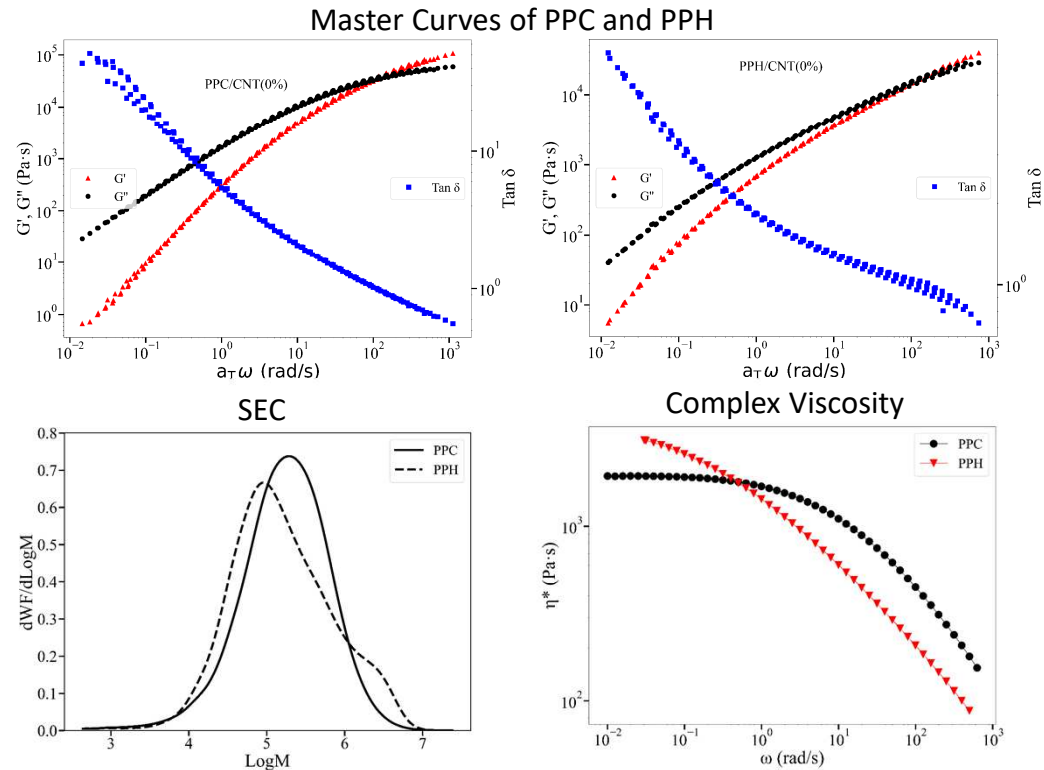
Figure 6. (a) Shear creep compliance,  $J_c$ , as a function of creep time for the neat materials (open symbols) and the nanocomposites (lines) at a shear stress of  $\tau_0 = 6.25\text{--}50\text{ Pa}$  and  $T = 140\text{ }^\circ\text{C}$ ; (b) Dynamic modulus,  $G'$ , versus angular frequency,  $\omega$ , of the neat materials (open symbols) and the nanocomposites (close symbols and lines) at  $T = 140\text{ }^\circ\text{C}$  (three independent measurements for each sample are plotted). (red ●, ○) PE1, (blue ▲, △) PE2 and (■, □) PE3.

Juan Francisco Vega, Yudith da Silva, Ernesto Vicente-Alique, Rafael Núñez-Ramírez, Mariselis Trujillo, María Luisa Arnal, Alejandro J. Müller, Philippe Dubois, and Javier Martínez-Salazar, *Macromolecules* **2014** 47 (16), 5668-5681, DOI: 10.1021/ma501269g

# Strategies and Methods

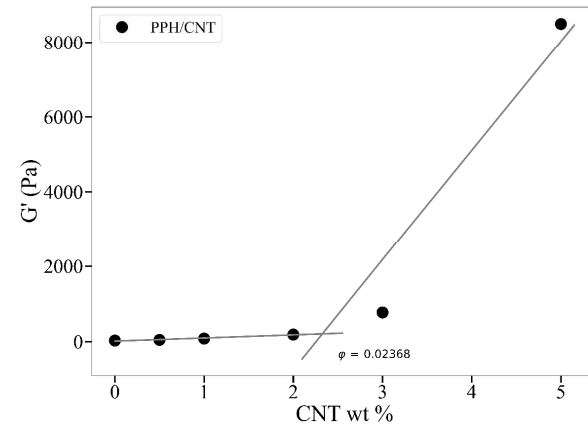
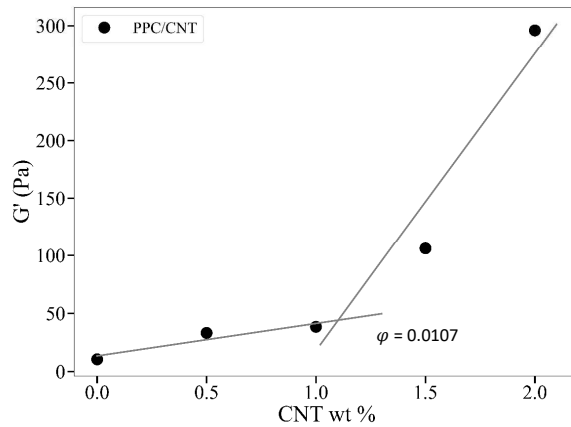
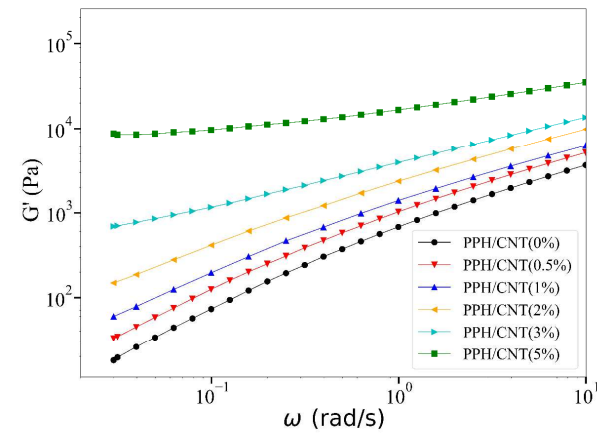
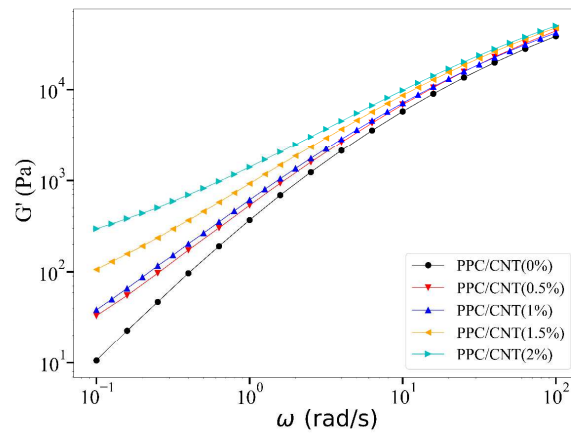


# Results: Comparison of PPC and PPH



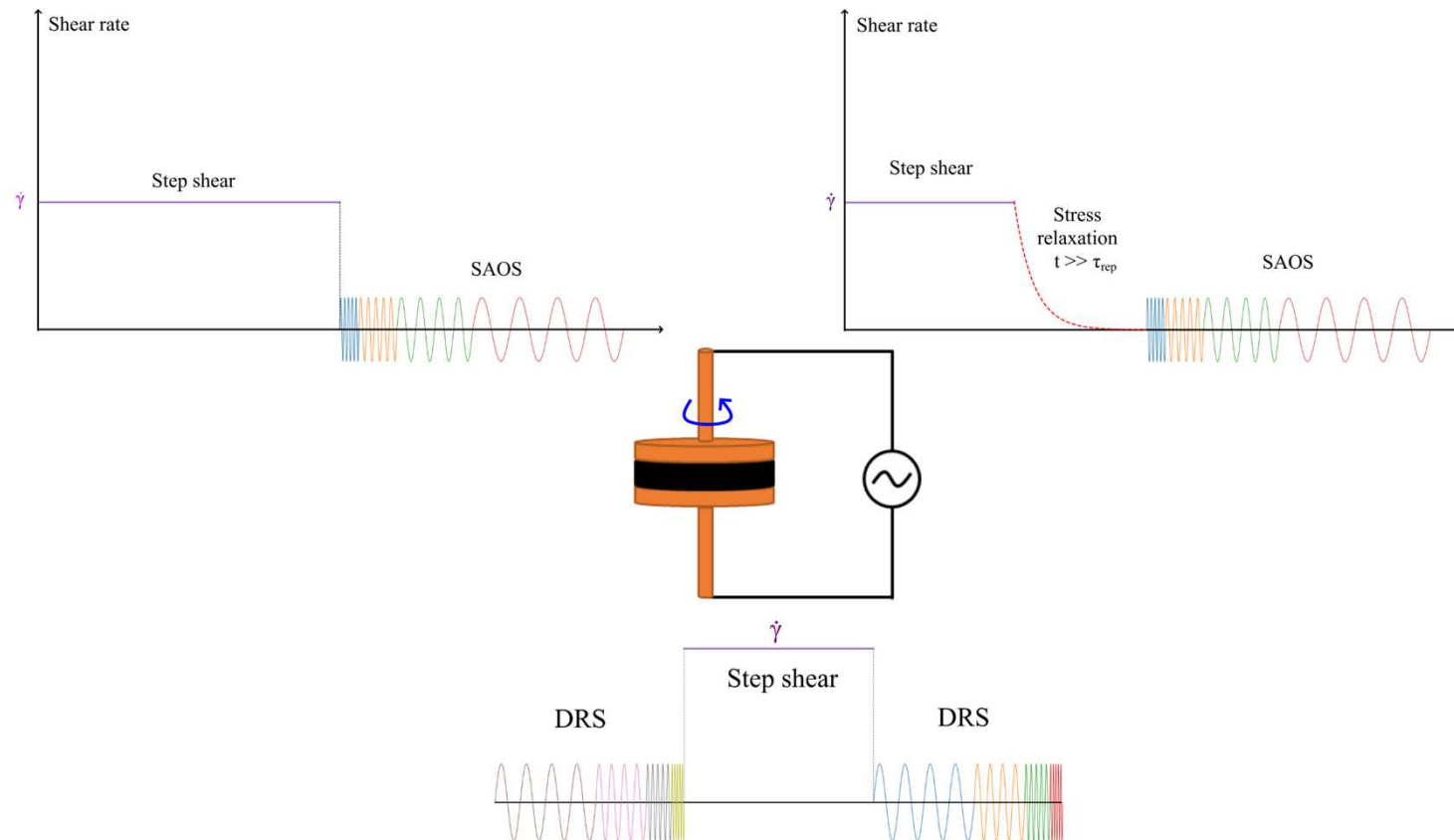
Polymer <sup>↙</sup>	$M_w$ (kg/mol) <sup>↙</sup>	$M_w/M_n$ <sup>↙</sup>	$\text{LCBf}/1000C$ <sup>↙</sup>	$\eta_0$ (pa.s) <sup>↙</sup>	$G_N^0$ (pa) <sup>↙</sup>	$M_e$ (g/mol) <sup>↙</sup>	$\tau_{rep}$ (s) <sup>↙</sup>
PPC <sup>↙</sup>	355 <sup>↙</sup>	6.9 <sup>↙</sup>	0 <sup>↙</sup>	$1.98 \times 10^3$ <sup>↙</sup>	$2.8 \times 10^5$ <sup>↙</sup>	4471 <sup>↙</sup>	$\sim 0.10$ <sup>↙</sup>
PPH <sup>↙</sup>	475 <sup>↙</sup>	9.8 <sup>↙</sup>	0.021 <sup>↙</sup>	$4.20 \times 10^3$ <sup>↙</sup>	$4.73 \times 10^6$ <sup>↙</sup>	253 <sup>↙</sup>	$\sim 5.03$ <sup>↙</sup>

# Results: Percolation of PPC and PPH at 200 °C



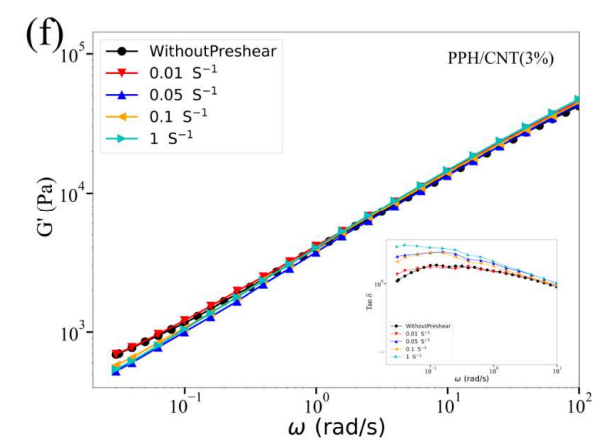
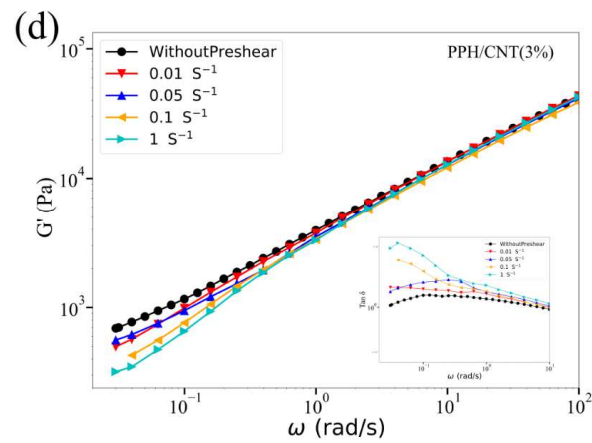
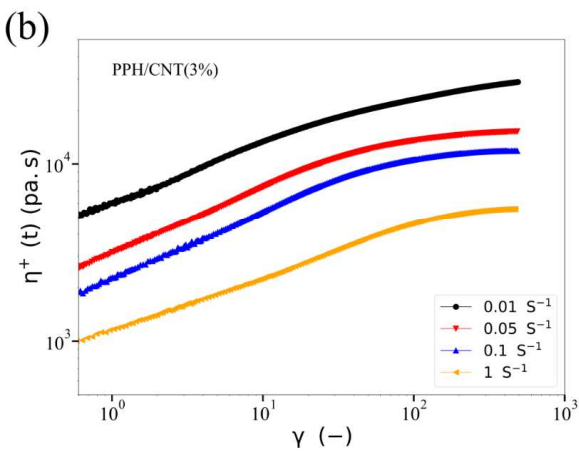
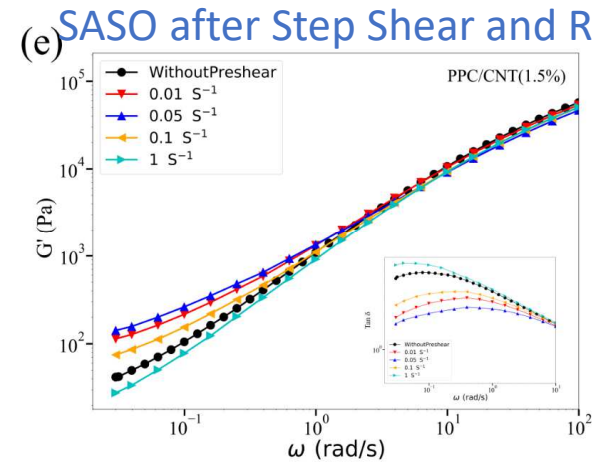
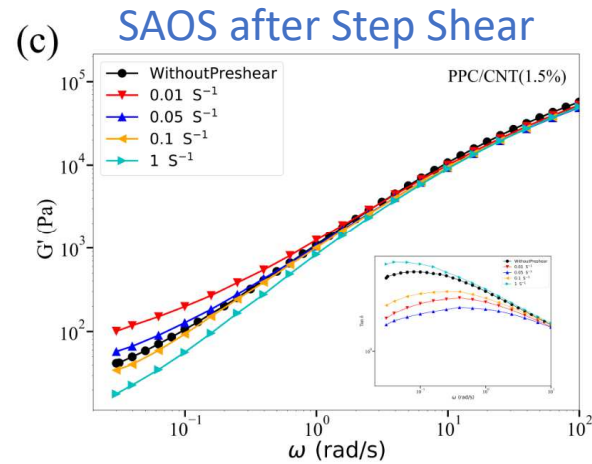
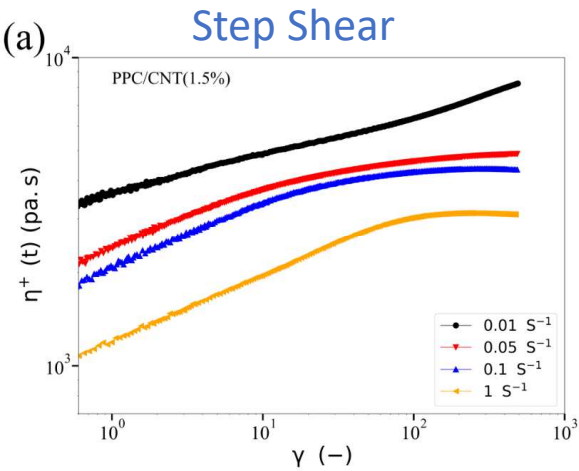


# Pre-shear Protocols

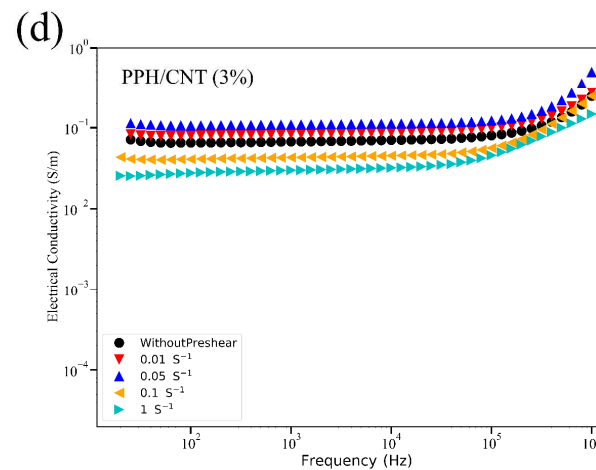
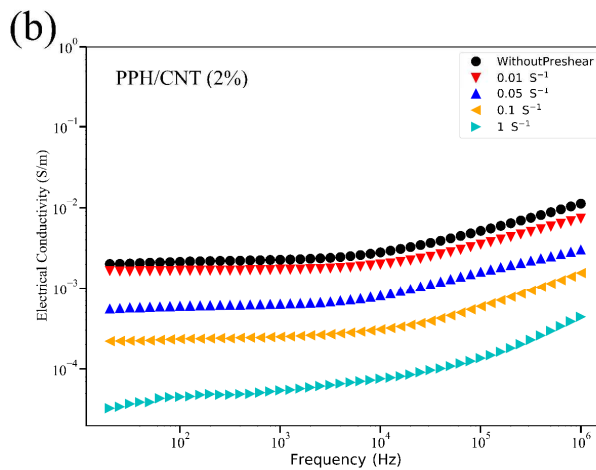
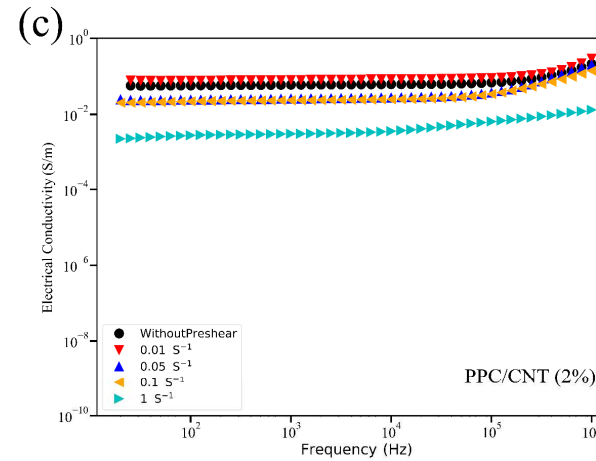
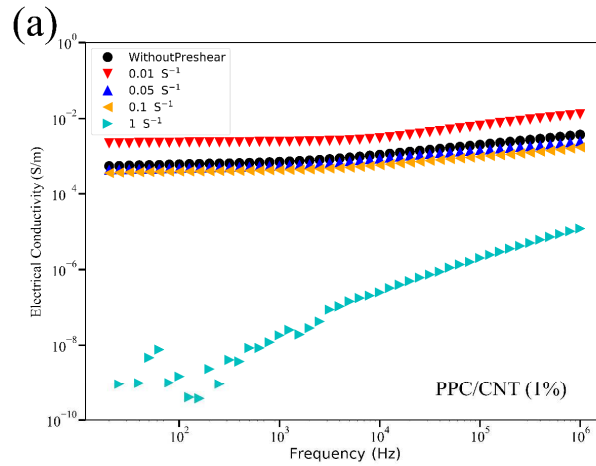


# Results: Liquid-solid transition after a pre-shear

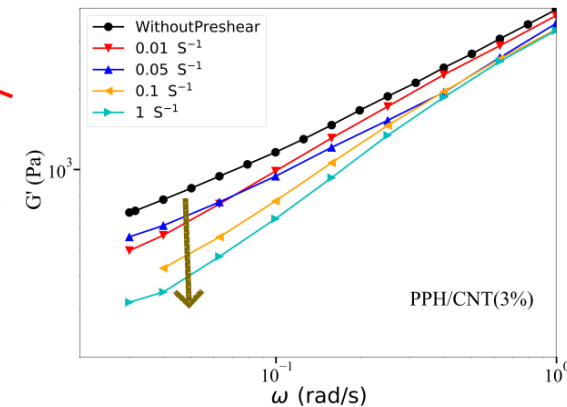
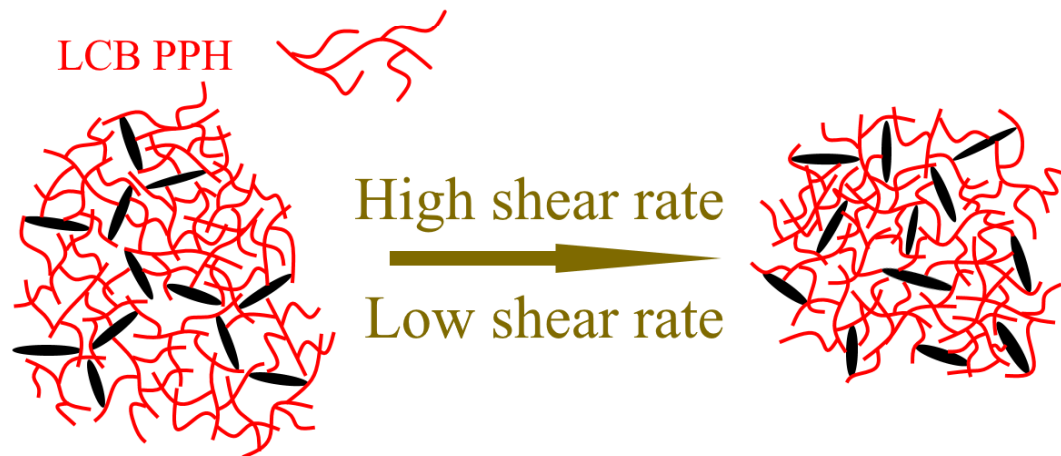
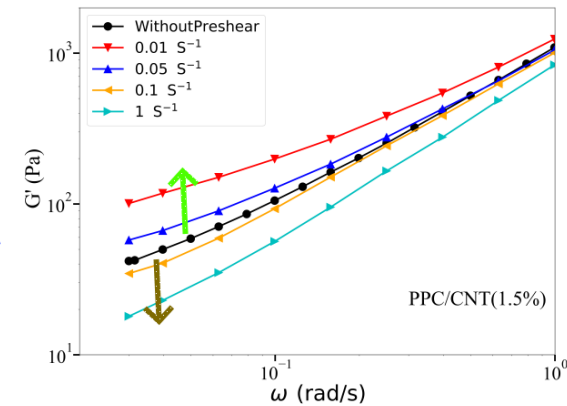
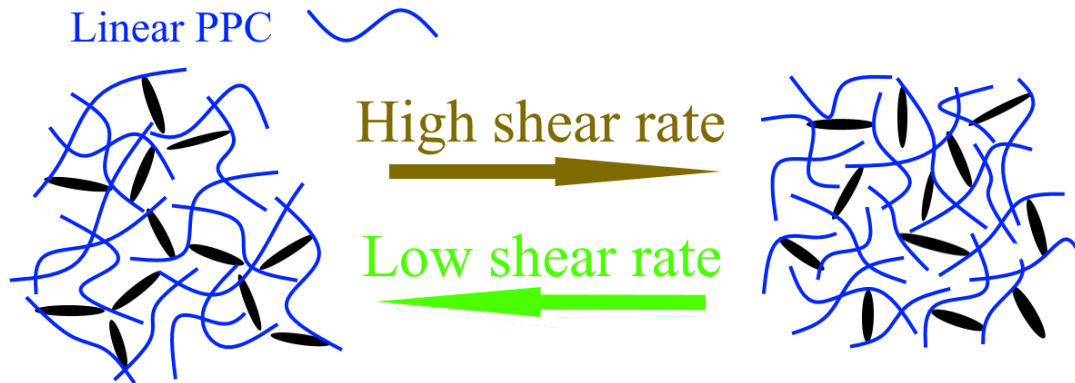
The samples with filler fraction higher than the percolation



# Results: Conductivities after a pre-shear



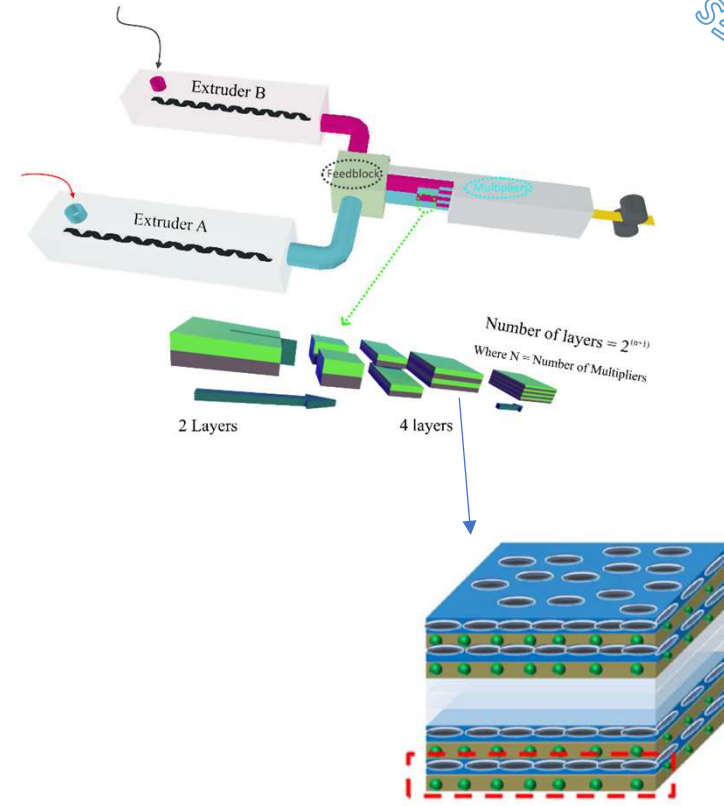
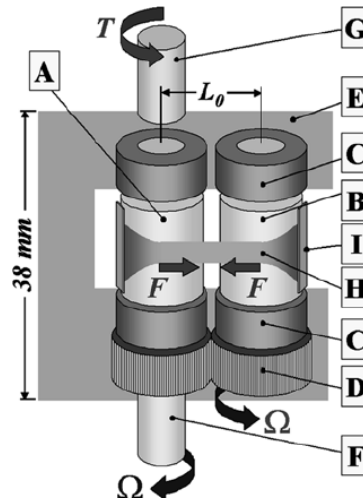
# CNT network aggregate and break down



# Perspectives

Next steps

1. Go deeper to analyze the phenomenon.
2. Nonlinear transient rheology on filled polymers
3. Work with different shape of fillers (Micro)
4. Start with co-extrusion



THANK YOU!!!



# Appendix



## NC7000™

Multiwall carbon nanotubes

### General Information

#### Description

NANOCYL® NC7000™ series, thin multiwall carbon nanotubes, are produced via the Catalytic Chemical Vapor Deposition (CCVD) process.

#### Key Applications

A primary interest is in applications requiring low electrical percolation threshold such as high-performance electrostatic dissipative plastics or coatings.

PROPERTIES	UNIT	VALUE	METHOD OF MEASUREMENT
<i>Average diameter</i>	10 <sup>-9</sup> m	9.5	Transmission Electron Microscopy (TEM)
<i>Average length</i>	µm	1.5	Transmission Electron Microscopy (TEM)
<i>Carbon purity</i>	%	90	Thermogravimetric analysis (TGA)
<i>Transition Metal oxide</i>	%	< 1%	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
<i>Amorphous carbon</i>	-	*	High resolution Transmission Electron Microscopy (HRTEM)
<i>Surface Area</i>	m <sup>2</sup> /g	250-300	BET surface area analysis
<i>Volume resistivity</i>	Ω.cm	10 <sup>-4</sup>	Internal test method (resistivity on powder)

\*Pyrolytically deposited carbon on the surface of the NC7000