有机无机复合材料国家重点实验室
State Key Laboratory of Organic-Inorganic Composites

聚合物纳米复合材料高性能化和功能化

于中振
北京化工大学
材料科学与工程学院

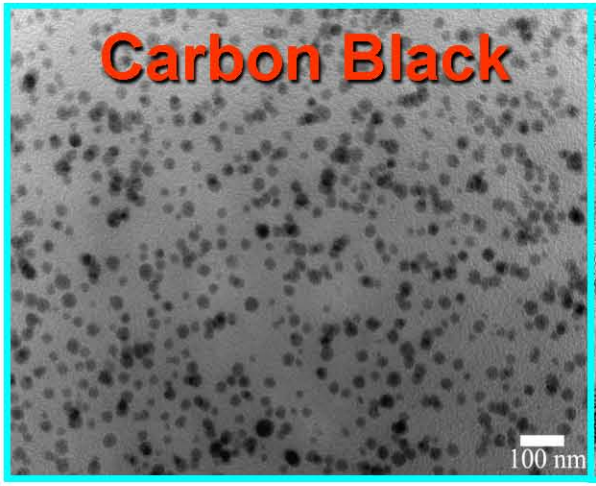
2014年创新复合材料应用高峰论坛
2014/08/20-21，上海

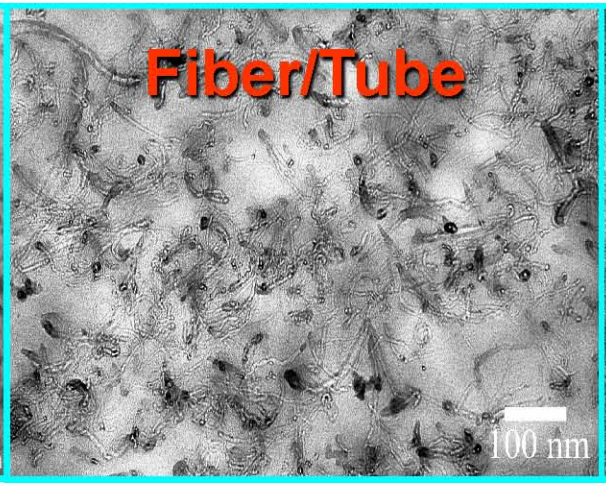
Conductive Fillers

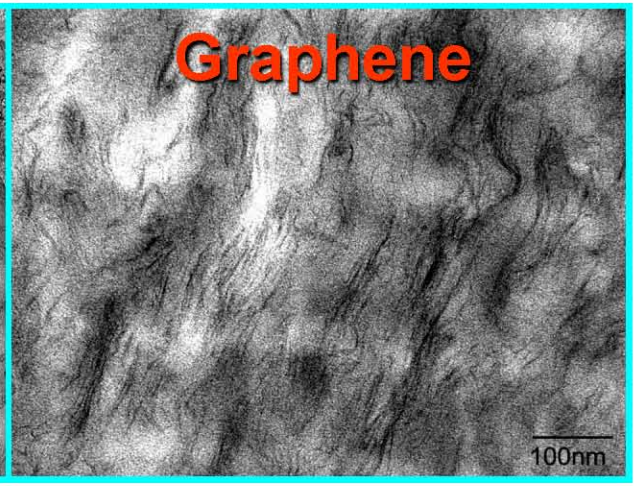
D < 100 nm

L < 100 nm

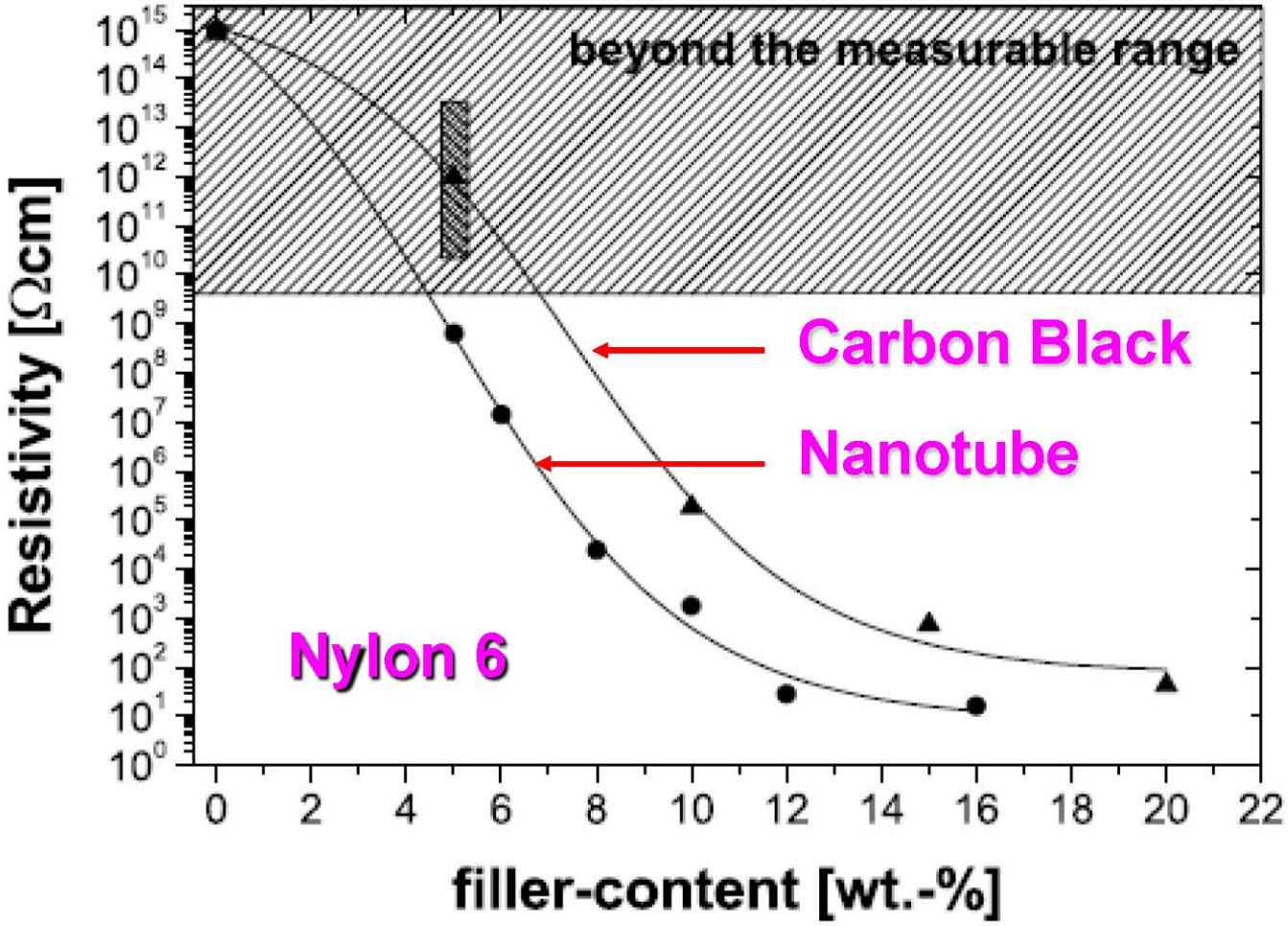
T < 100 nm





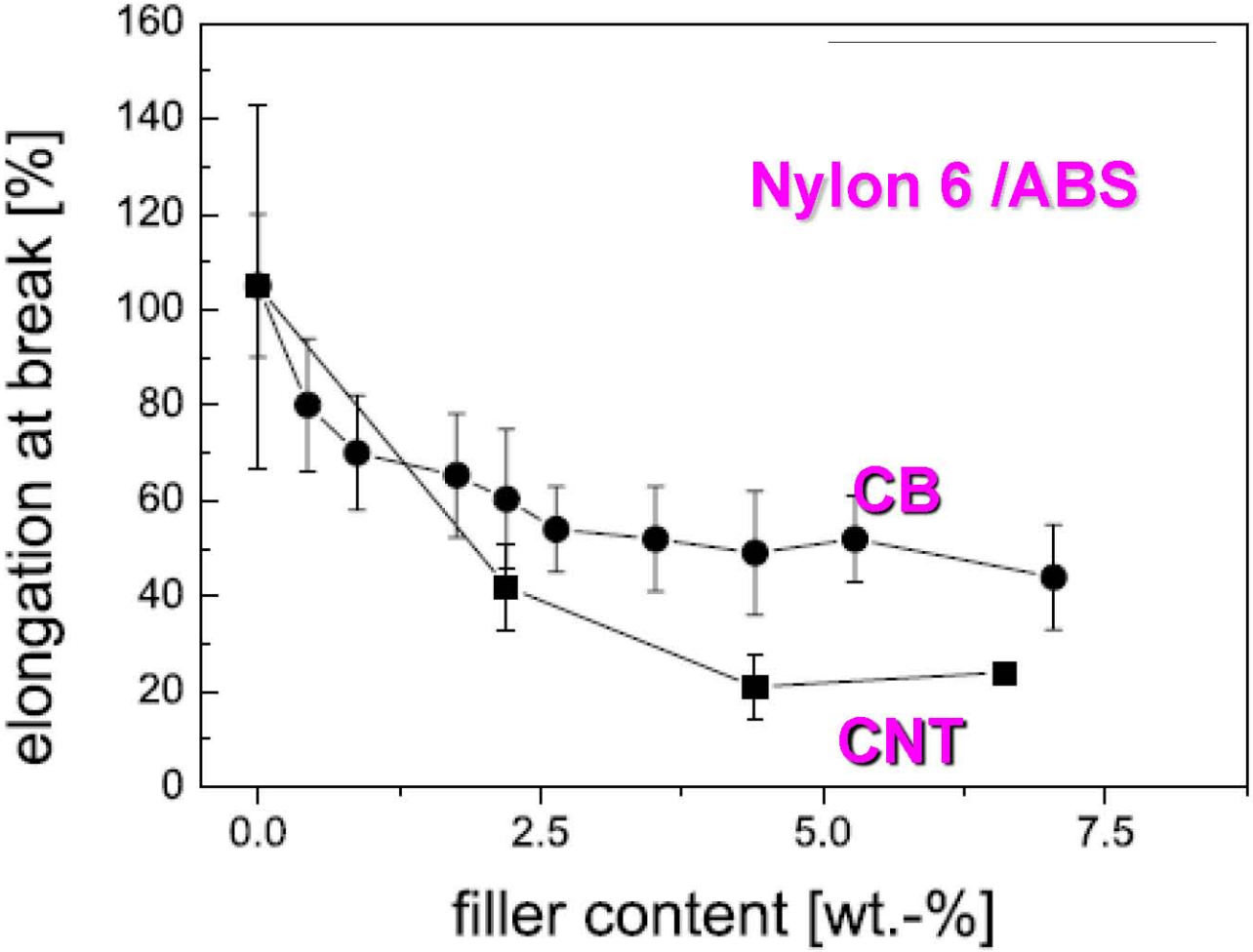


Increased Conductivity



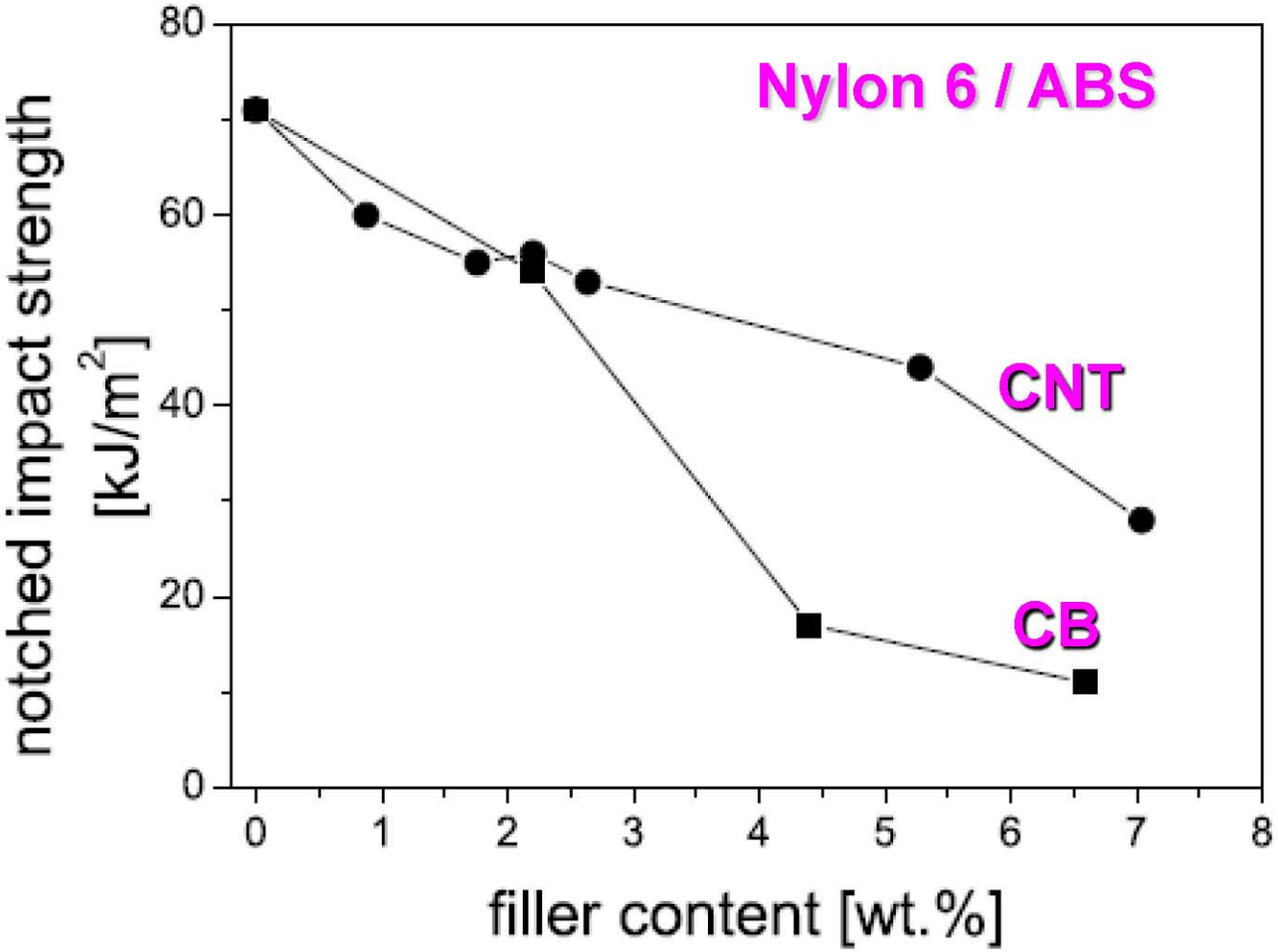
Meincke O, et al. Polymer 2004, 45, 739

Reduced Ductility



Meincke O, et al. Polymer 2004, 45, 739

Reduced Toughness



Meincke O, et al. Polymer 2004, 45, 739

Approach to Decrease Filler Loading

- **Blended with an immiscible polymer**

  PP / CB + PS

- **Filled with an insulating filler**

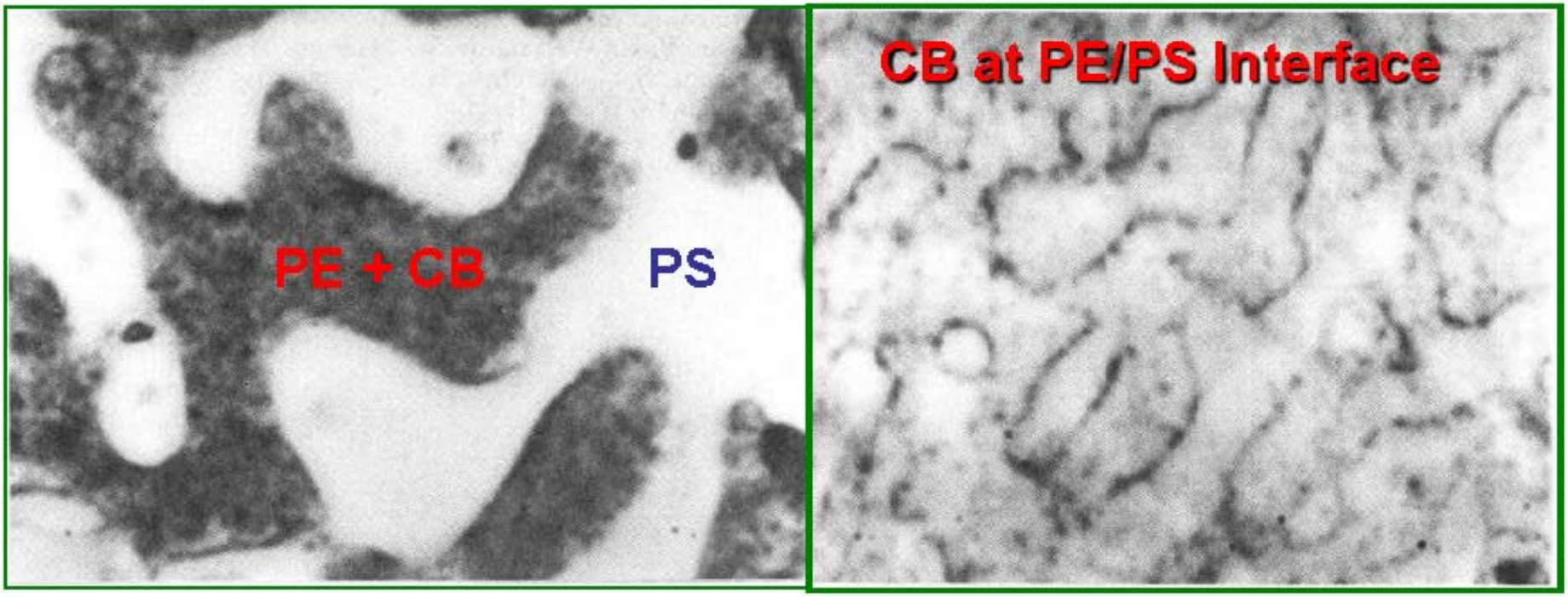
  PP / CB + $CaCO_3$

- **Use two conducting fillers**

  PP / CB + CNT

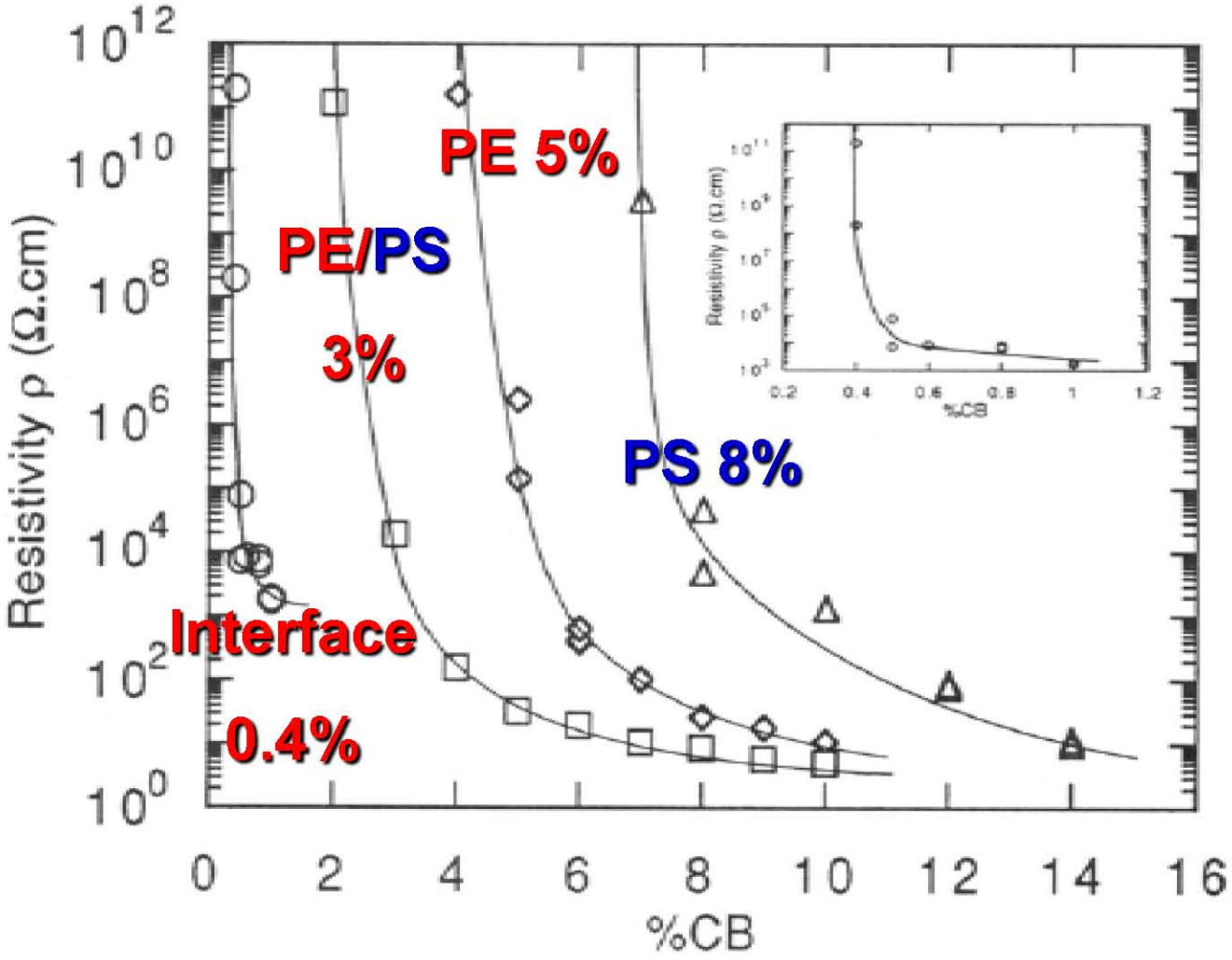
Blended with an Immiscible Polymer

PE/PS (45/55) Cocontinuous Blend with 1% Carbon Black



Gubbels F, et al. Macromolecules 1994, 27, 1972

Selective Localization of CB



Gubbels F, et al. Macromolecules 1994, 27, 1972

Approach to Decrease Loading of Filler

- Blended with an immiscible polymer

  PP / CB + PS

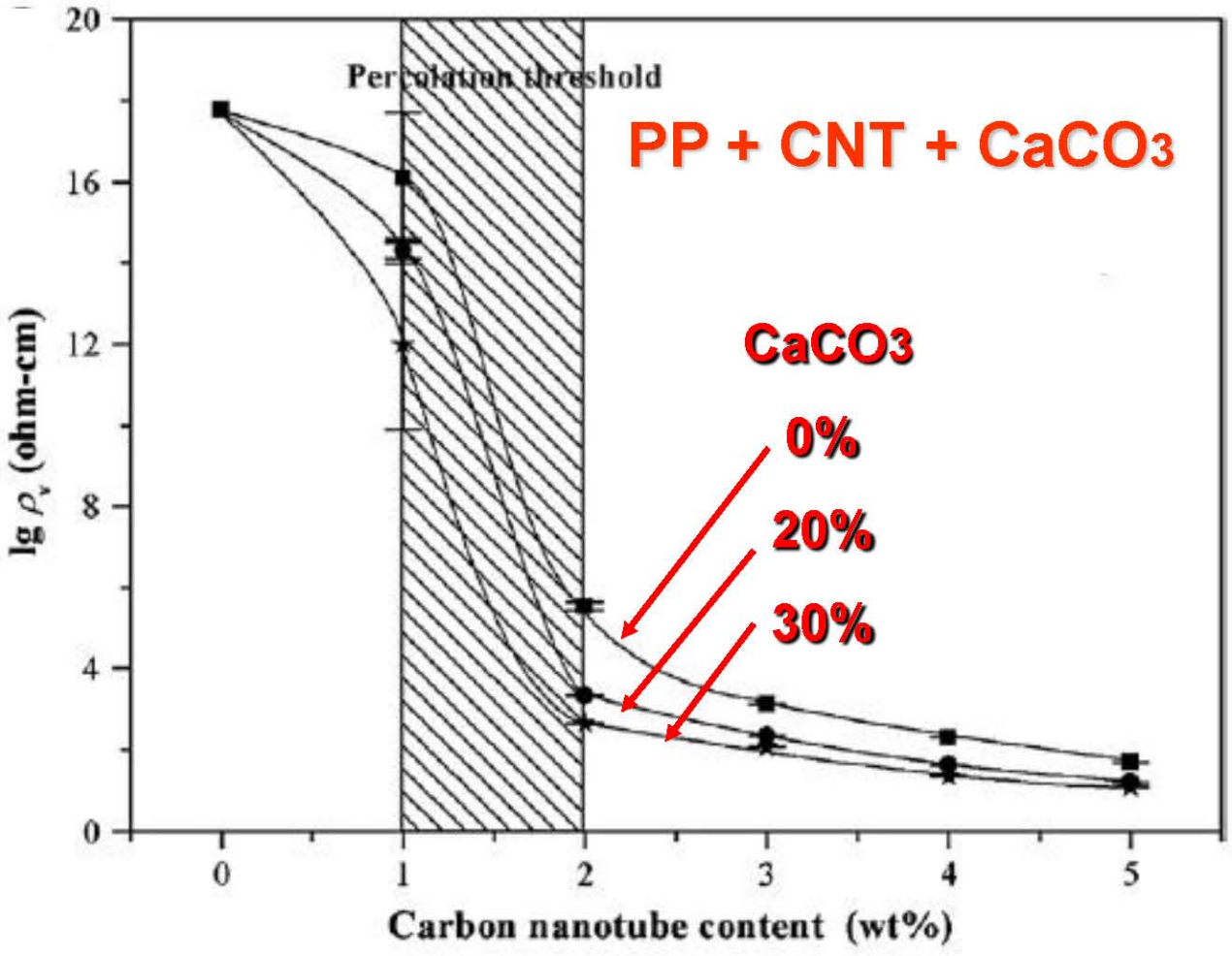
- **Filled with an insulating filler**

  PP / CNT + $CaCO_3$

- Use two conducting fillers

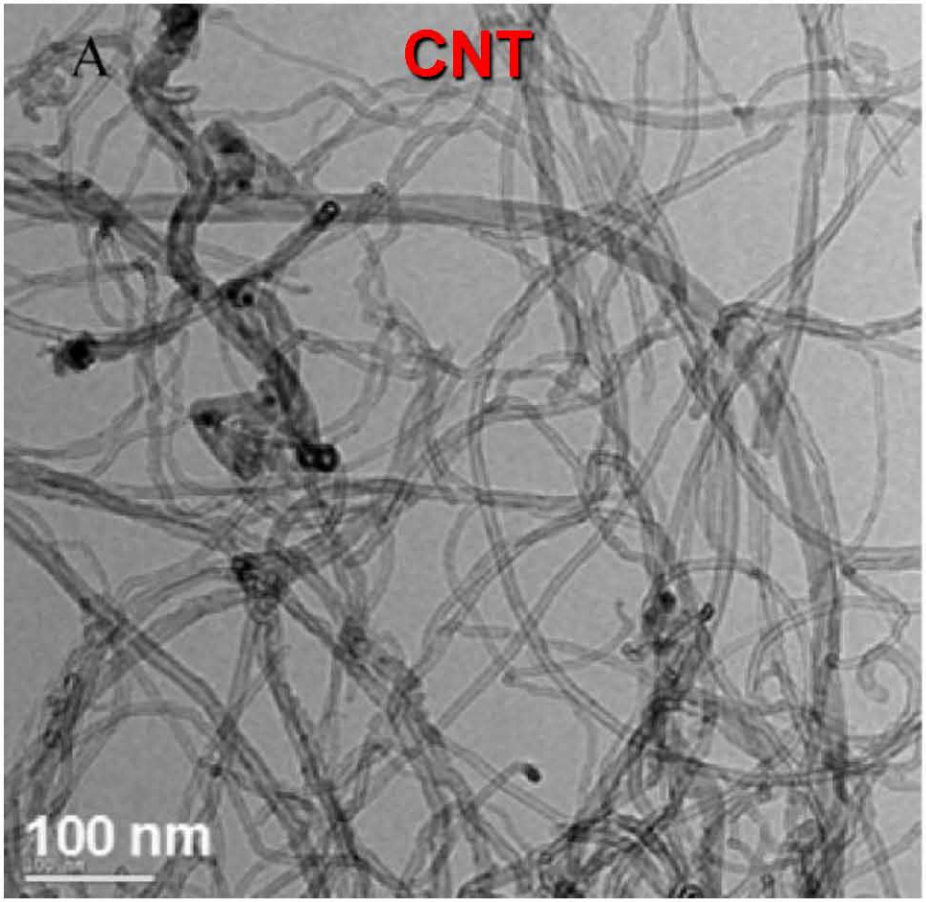
  PP / CB + CNT

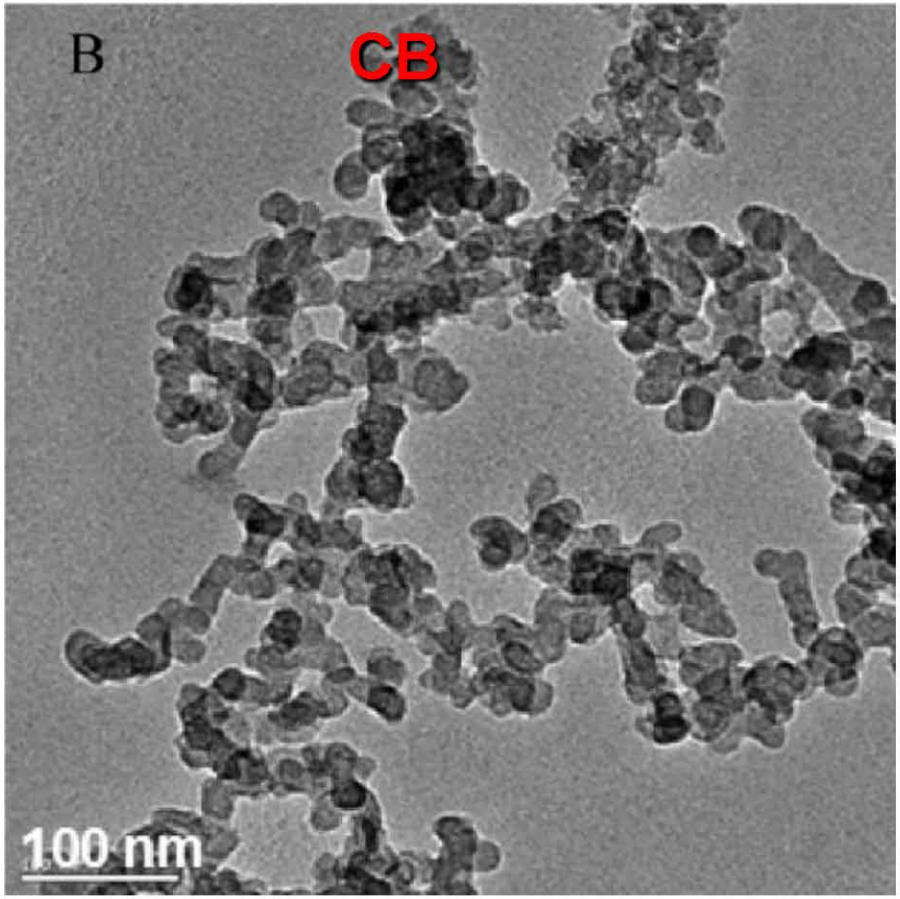
Filled with an Insulating Filler



Yu J, et al. Polymer 2008, 49, 3826

Using Two Conducting Fillers

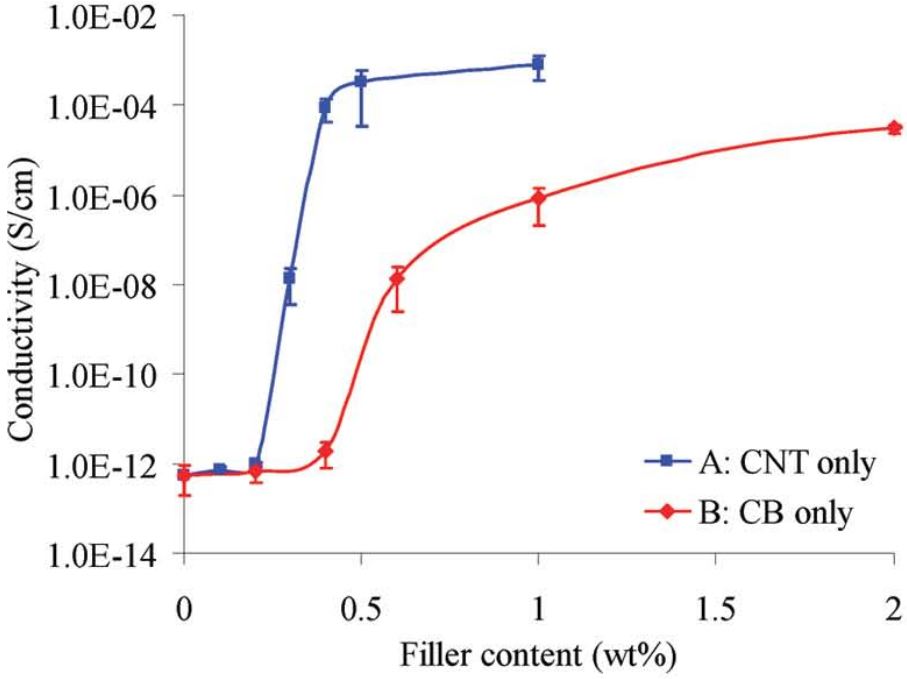


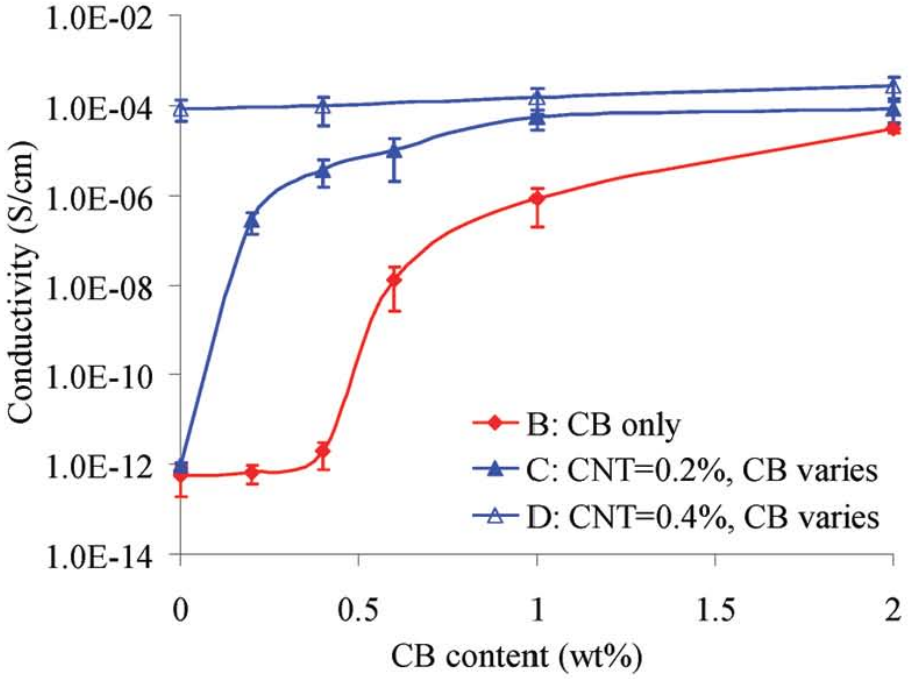


Kim JK, et al. ACS Appl. Mater. Interfaces 2009, 1, 1090

Using Two Conducting Fillers

Epoxy / CB / CNT





Kim JK, et al. ACS Appl. Mater. Interfaces 2009, 1, 1090

Embrittlement

- **blended with an immiscible polymer**

  PP / CB + PS

- **Filled with an insulating filler**

  PP / CB + CaCO3

- **Use two conducting fillers**

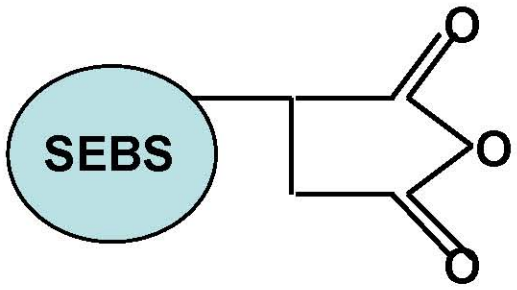
  PP / CB + CNT

Purposes

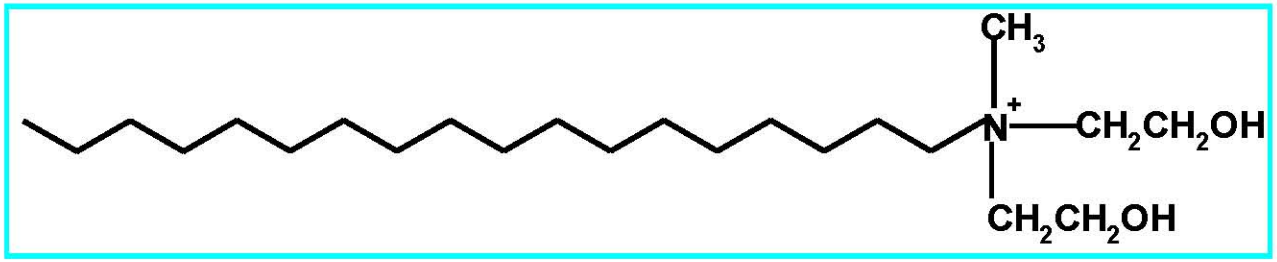
- make a polymer conductive and super-tough
- Reduce loading of conductive filler

1. Toughening of Nanocomposites

- Nylon 66
- Toughener: SEBS-g-MA



- Organoclay: Cloisite® 30B



Effect of Blending Sequence

- **B0: Nylon 66**

- **Binary Nanocomposites**

  B1: Nylon 66/Organoclay (80/5)

  B2: Nylon 66/SEBS-g-MA (80/15)

- **Ternary Nanocomposites**

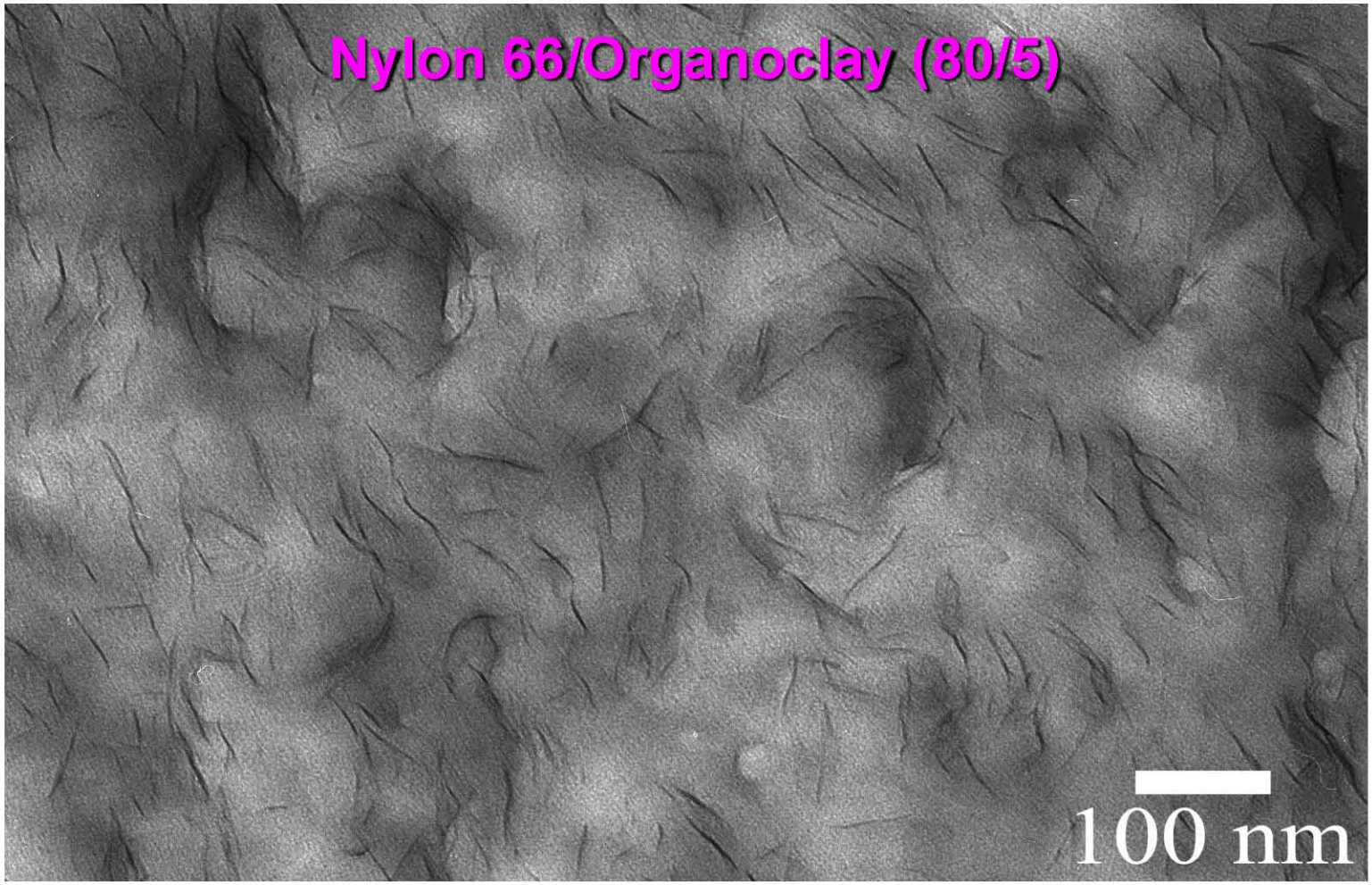
  N1: (Nylon 66 + SEBS-g-MA + Organoclay) (80/15/5)

  N2: (Nylon 66 + SEBS-g-MA) + Organoclay (80/15/5)

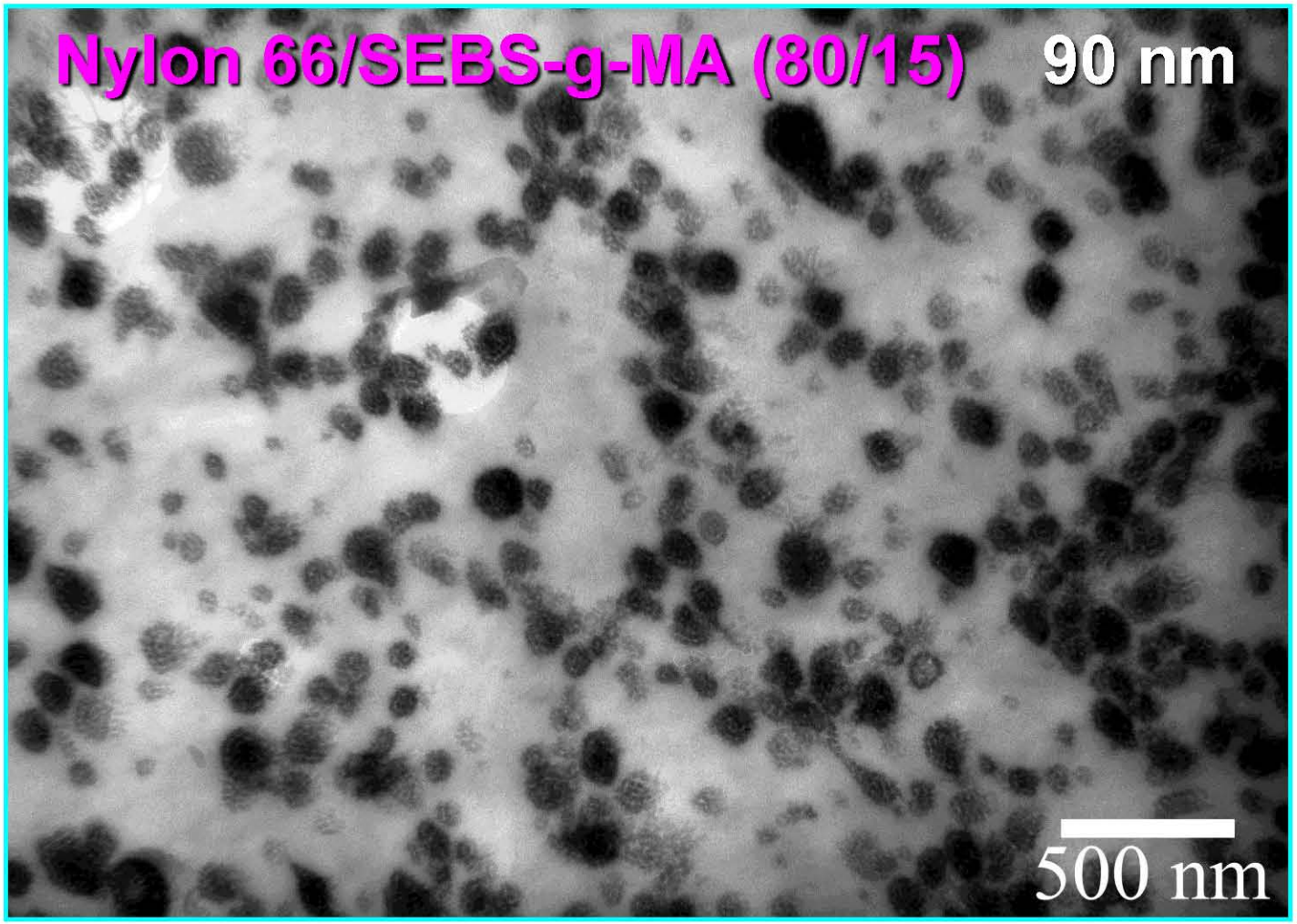
  N3: (Nylon 66 + Organoclay) + SEBS-g-MA (80/5/15)

  N4: Nylon 66 + (SEBS-g-MA + Organoclay) (80/15/5)

Binary Nanocomposite (B1)

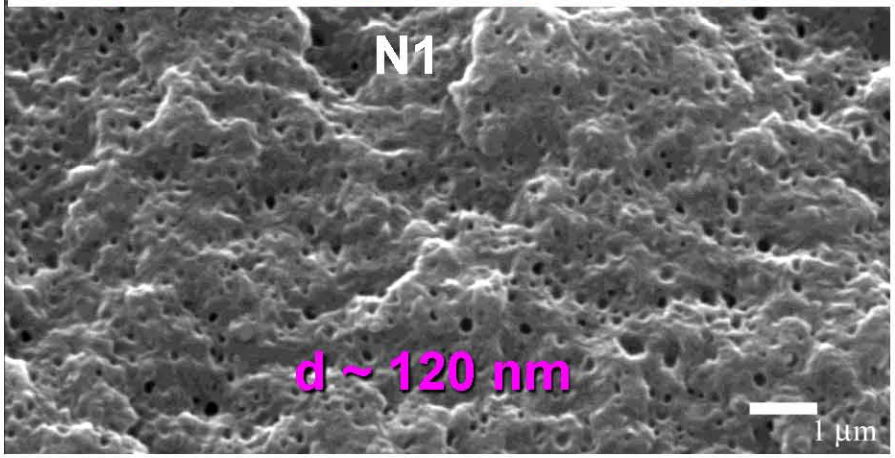


Binary Blend (B2)

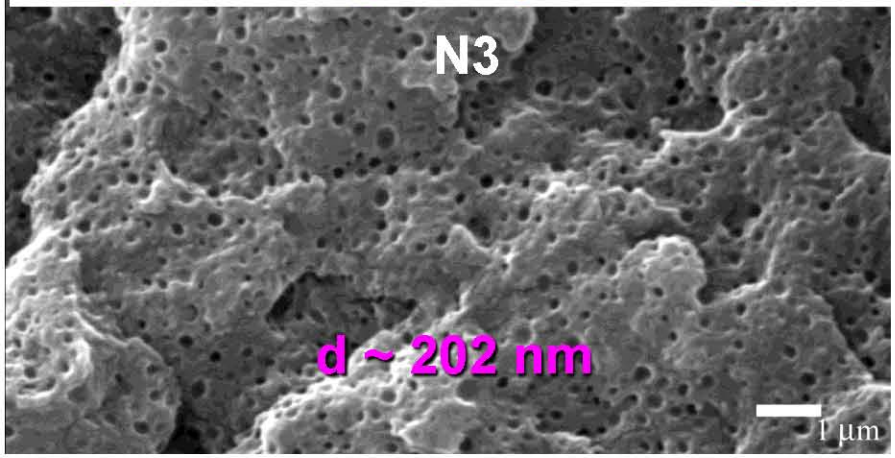


Dispersion of SEBS-g-MA

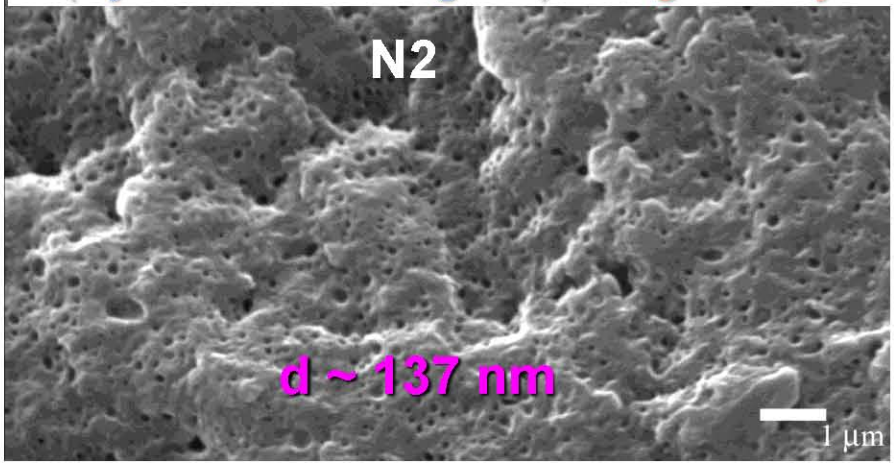
Nylon 66 + Organoclay + SEBS-g-MA



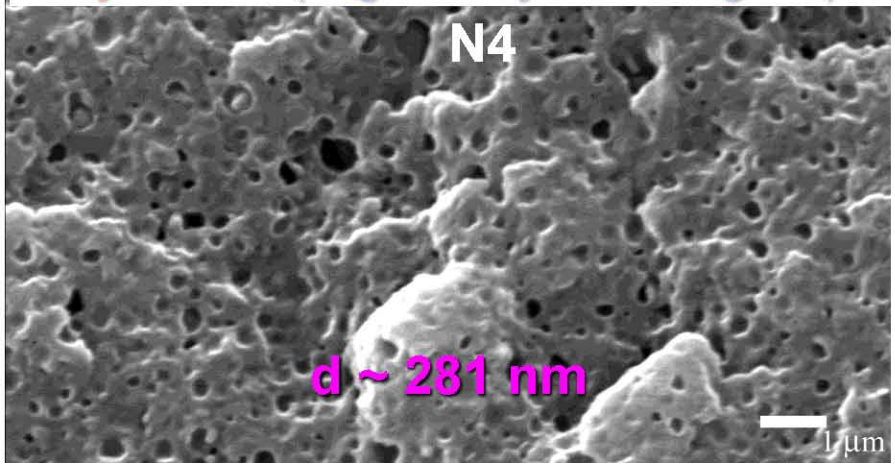
(Nylon 66 + Organoclay) + SEBS-g-MA



(Nylon 66 + SEBS-g-MA) + Organoclay

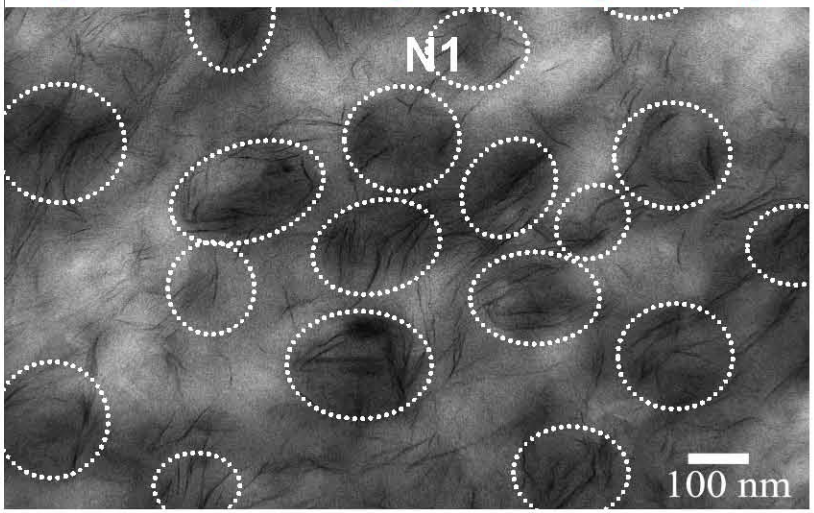


Nylon 66 + (Organoclay + SEBS-g-MA)

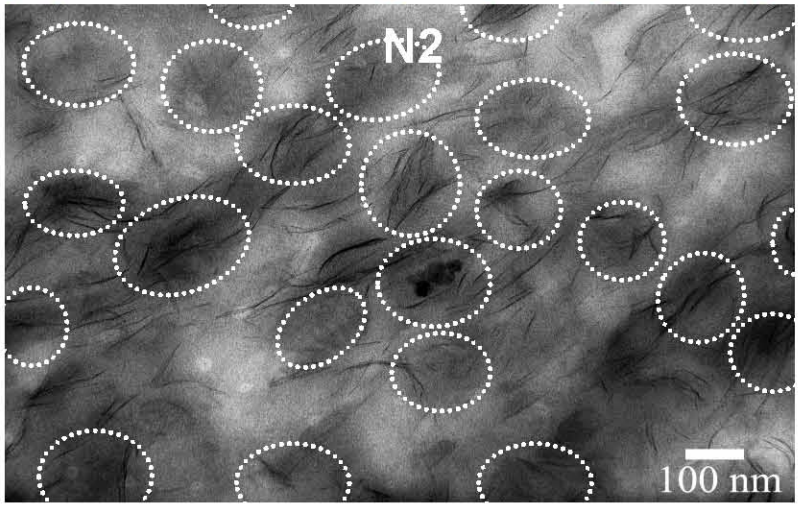


Location and Exfoliation of Clay

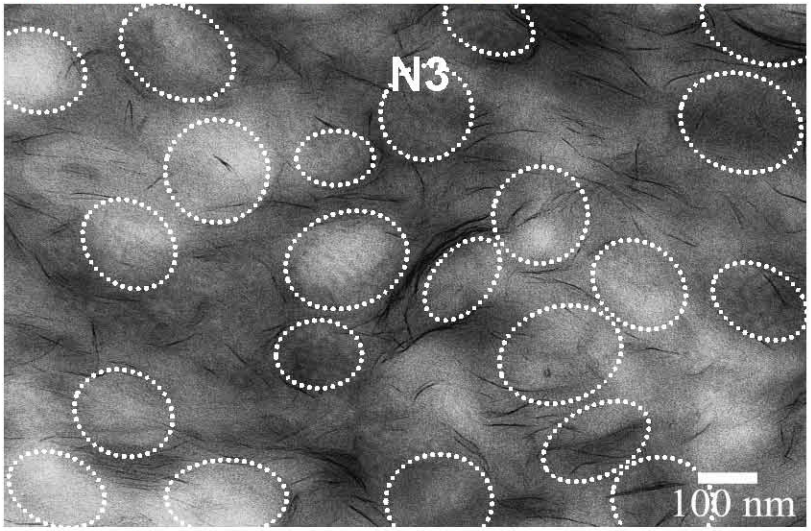
Nylon 66 + SEBS-g-MA + Organoclay



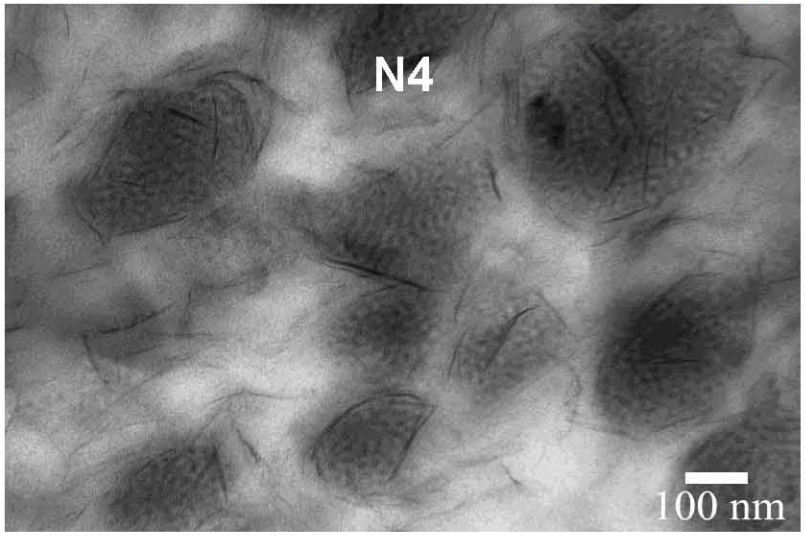
(Nylon 66 + SEBS-g-MA) + Organoclay



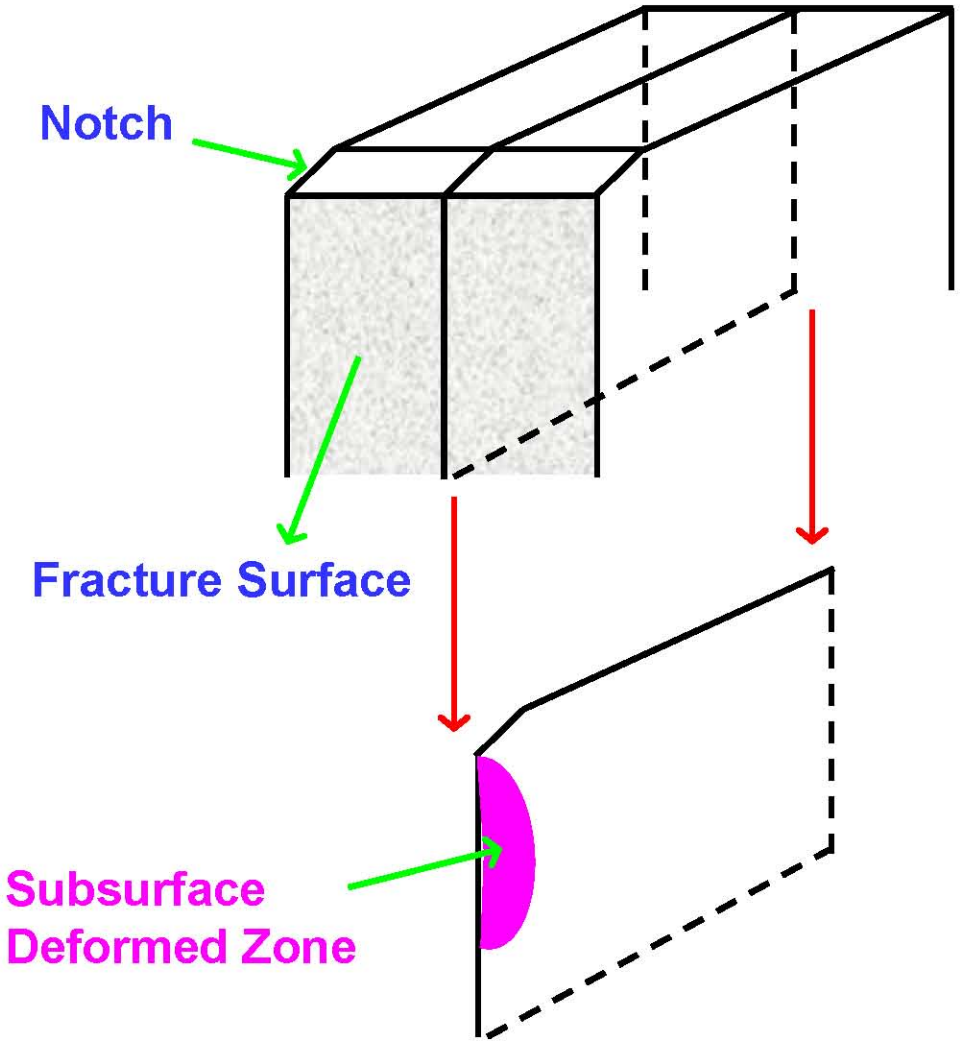
(Nylon 66 + Organoclay) + SEBS-g-MA



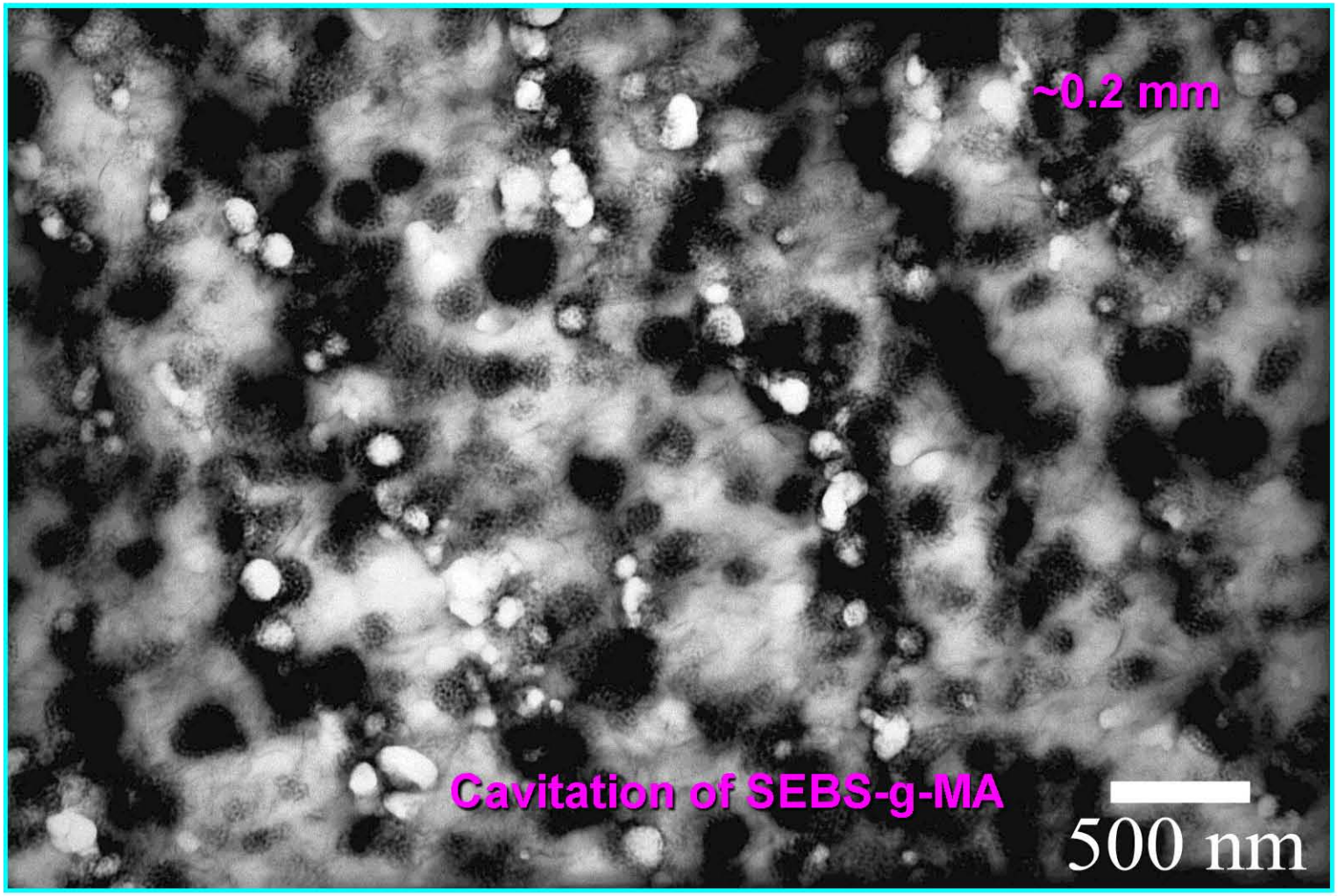
Nylon 66 + (SEBS-g-MA + Organoclay)



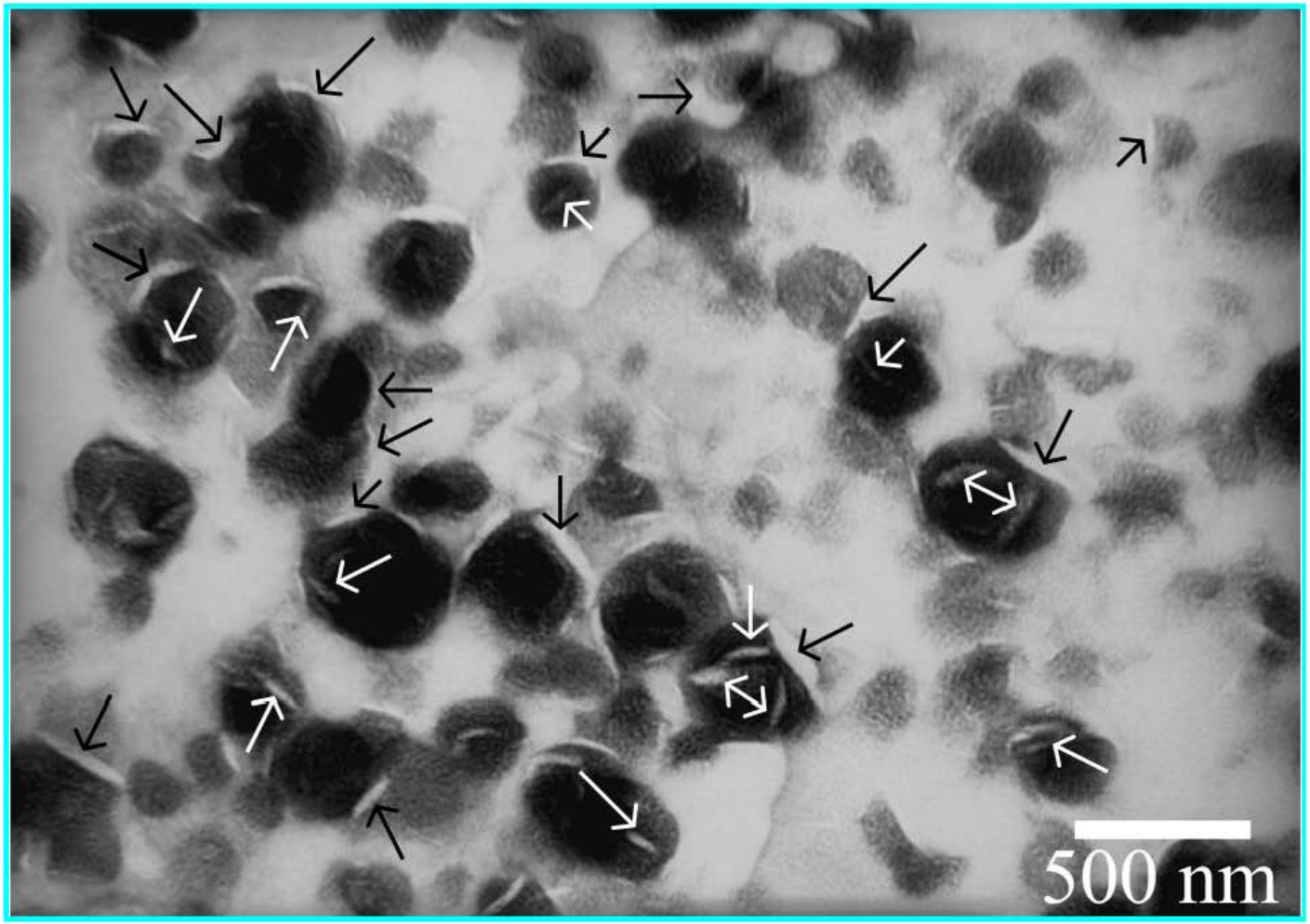
Sub-Surface Deformation



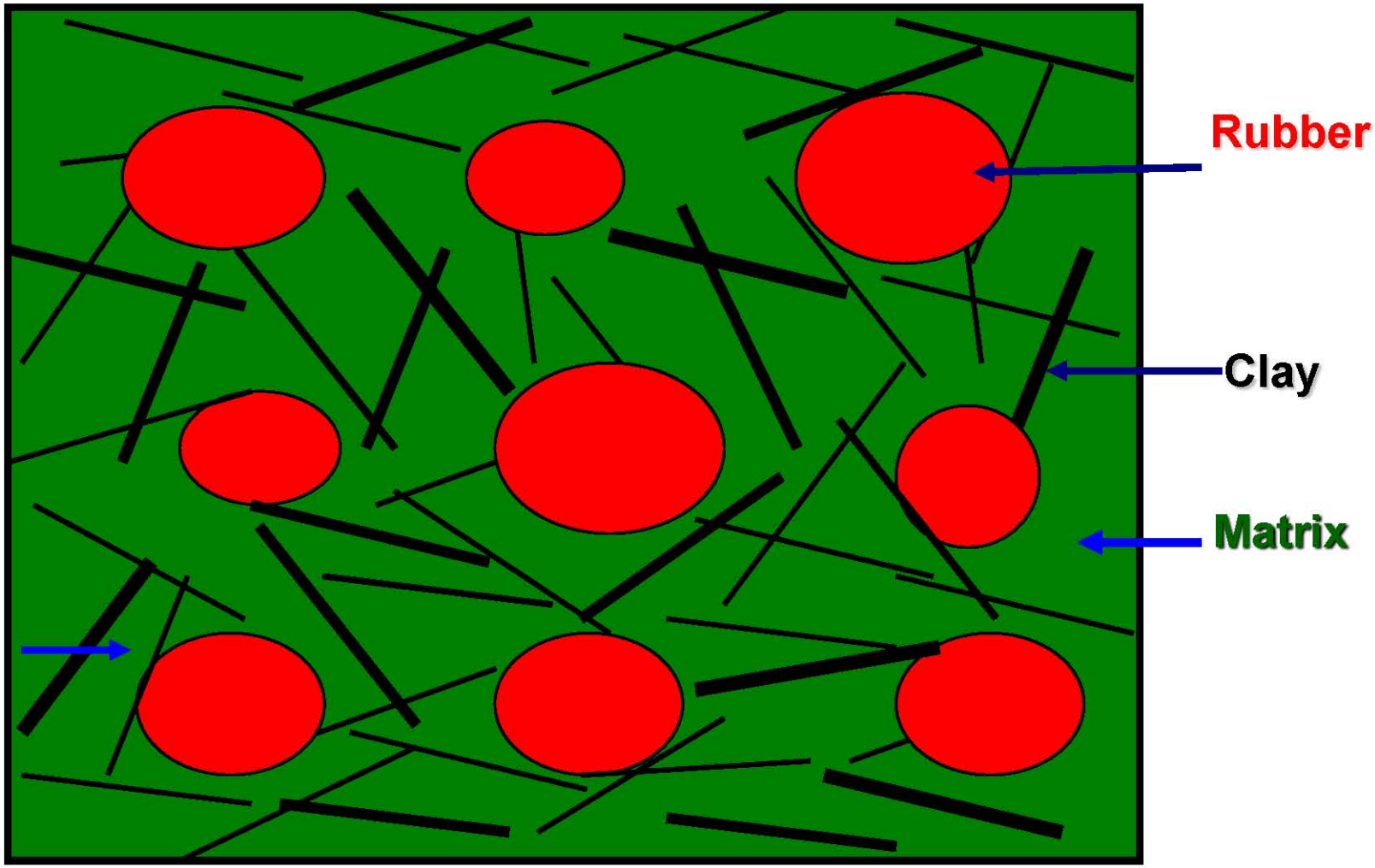
N3: (Nylon 66+Clay)+SEBS-g-MA



N4: Nylon 66+(Clay+SEBS-g-MA)

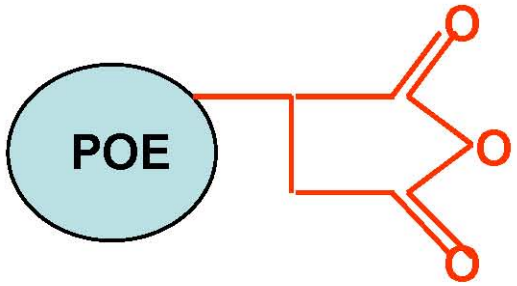


Ideal Microstructure

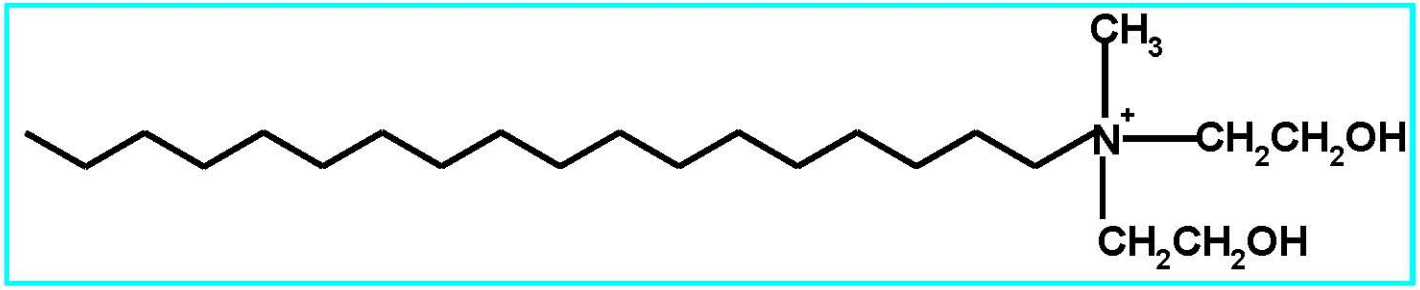


2. Formation of Such a Microstructure By One-Step Extrusion

- **Matrix:** Nylon 6
- **Toughener:** Maleated polyethylene-octene copolymer (POE-g-MA, 0.6 wt%)



- **Organoclay:** Cloisite® 30B

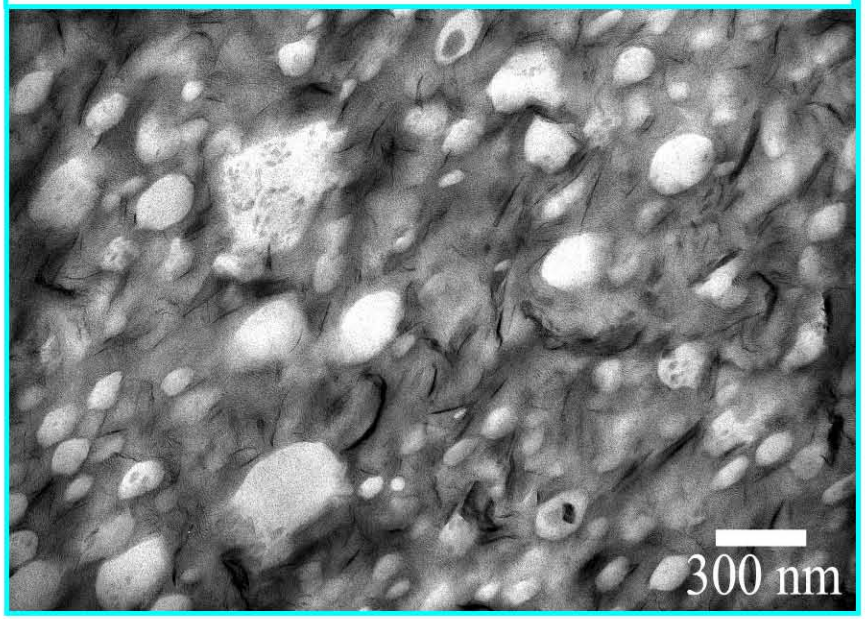


Nylon 6/Organoclay/POE-g-MA *Ternary* Nanocomposite

One-Step

Nylon 6 + Organoclay + POE-g-MA

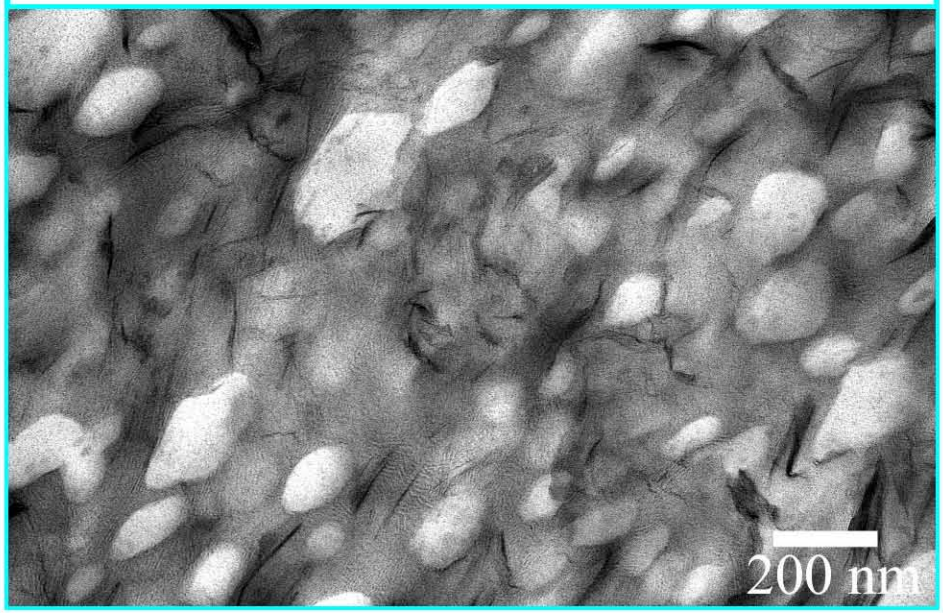
(76 / 4 / 20)



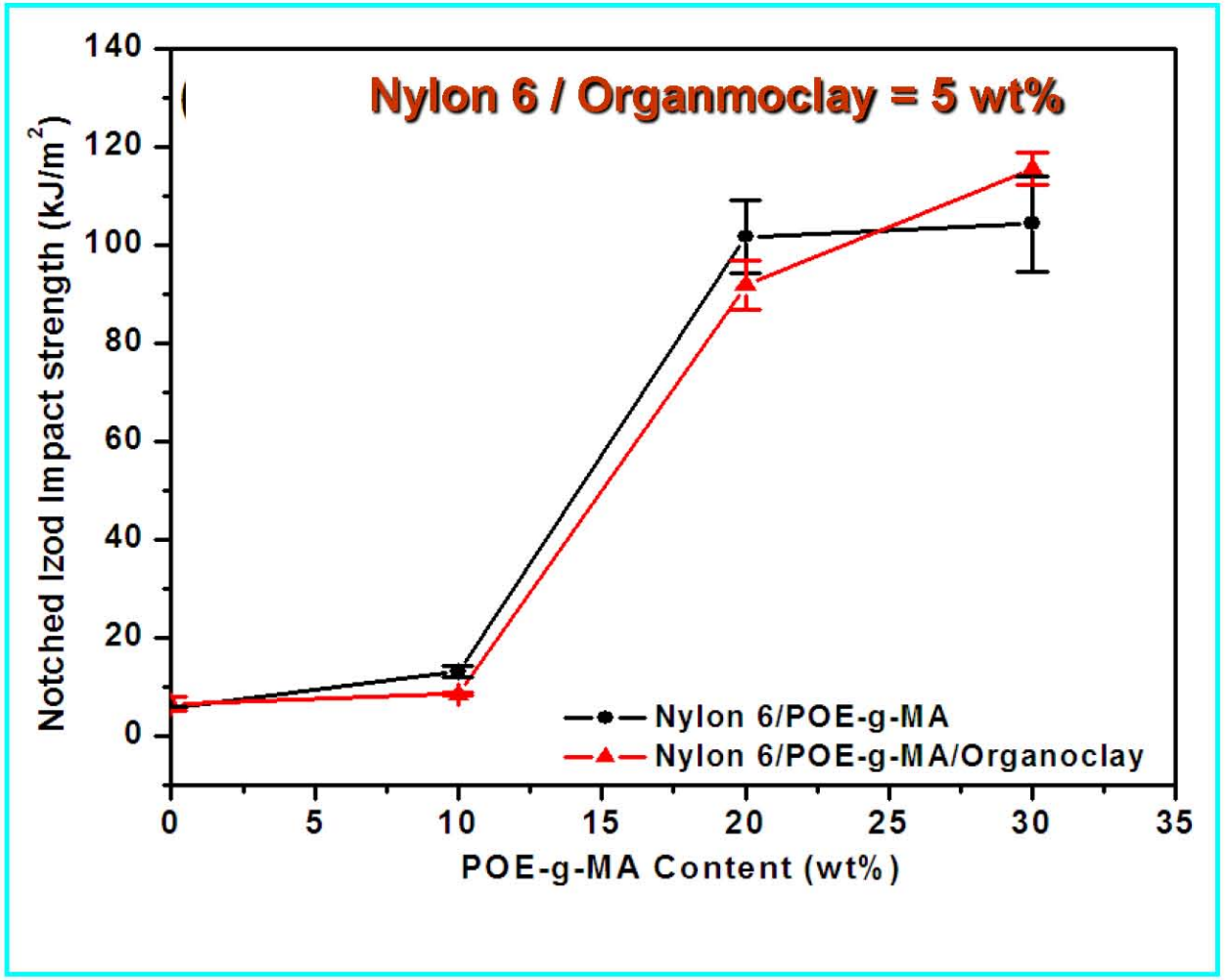
Two-Step

(Nylon 6 + Organoclay) + POE-g-MA

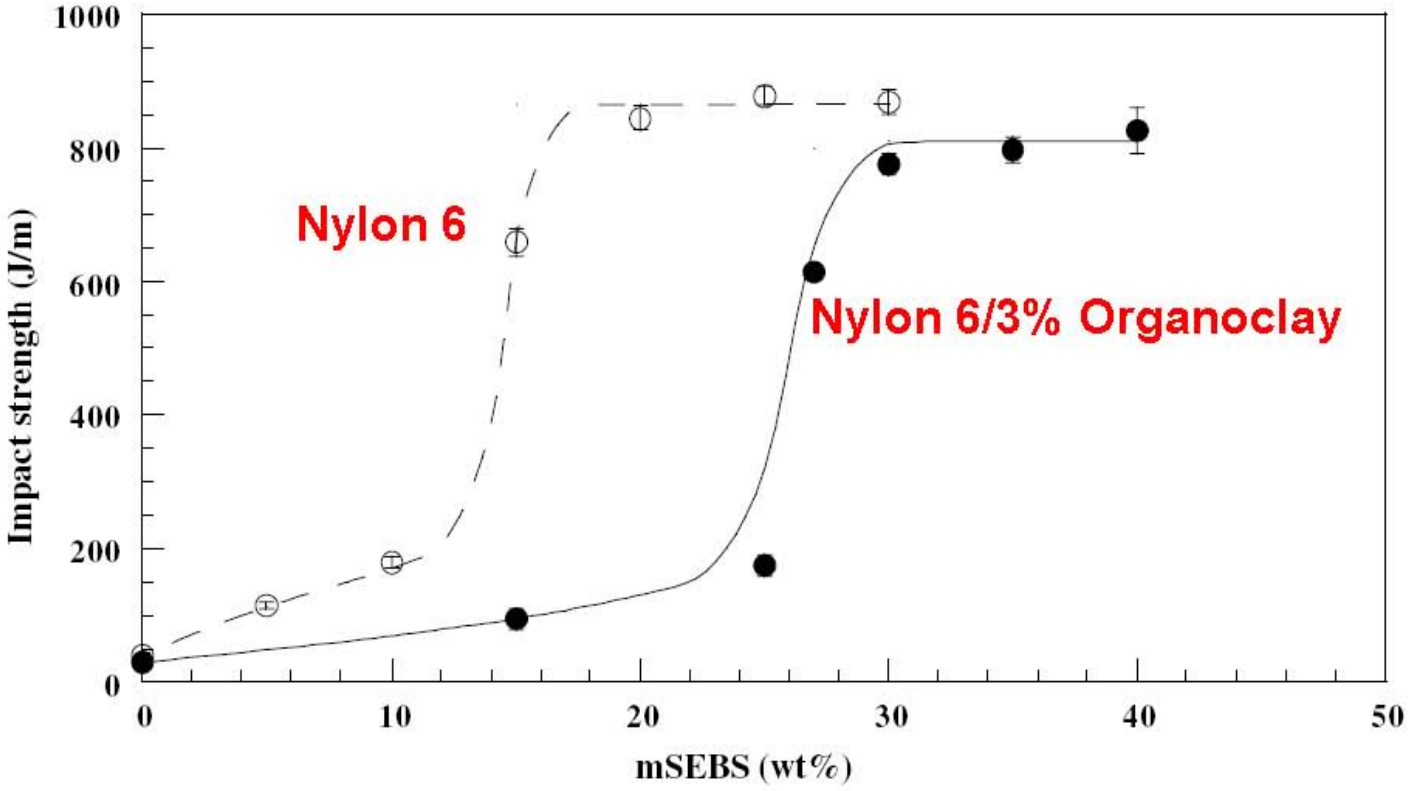
(72 / 8 / 20)



Toughening Efficiency of Rubber



Comparison with Literature

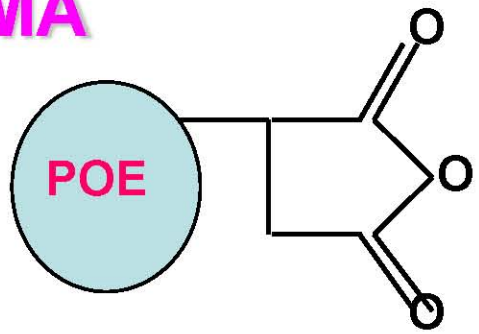


- Two-step melt extrusion
- (Nylon 6 / 3% Organoclay) + SEBS-g-MA

Nazabal J. et al. Composites Science and Technology 2006, 66, 1833

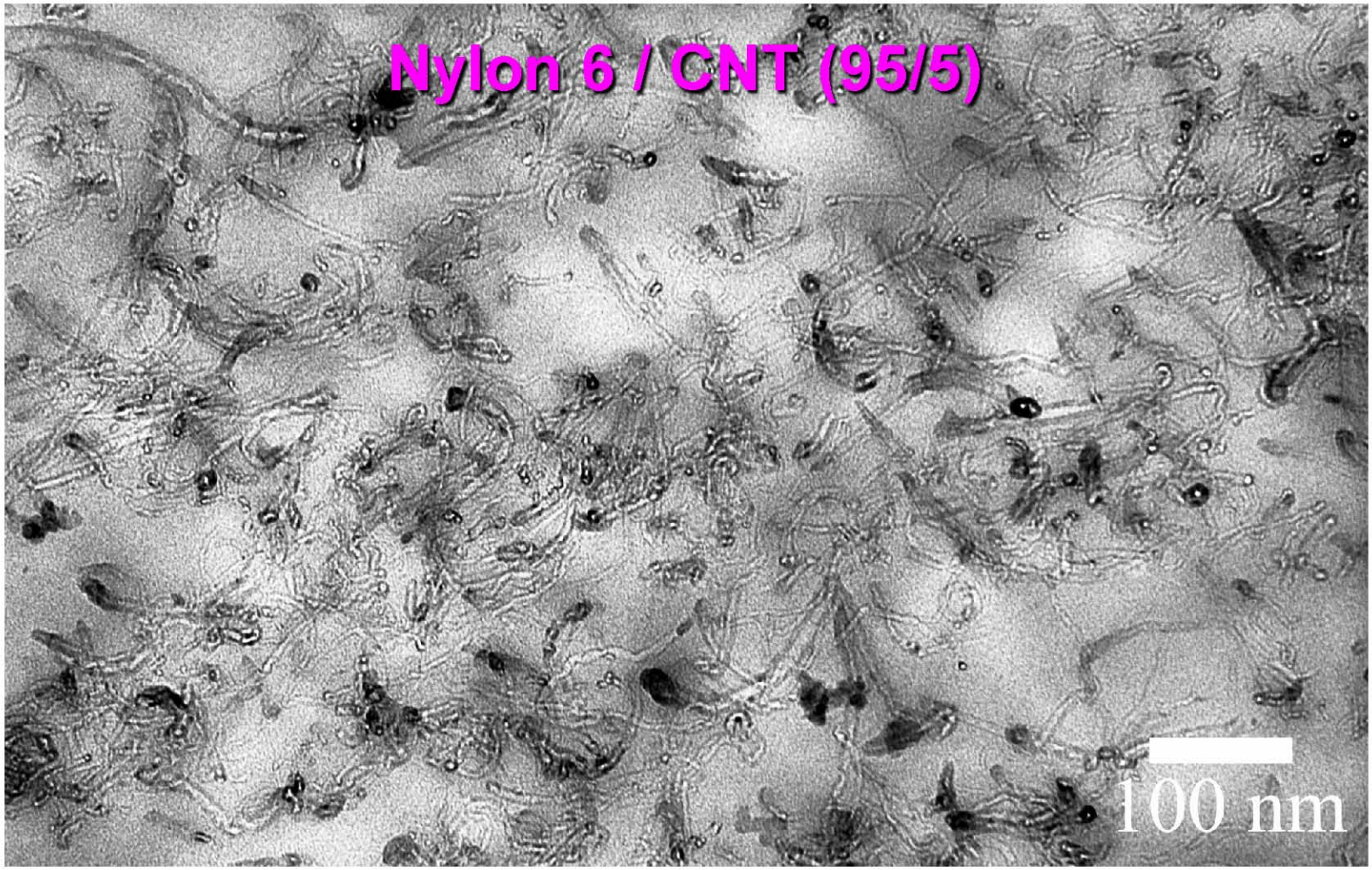
3. Electrically Conductive and Super-tough Nanocomposites

- **Matrix: Nylon 6**
- **Toughener: POE-g-MA**

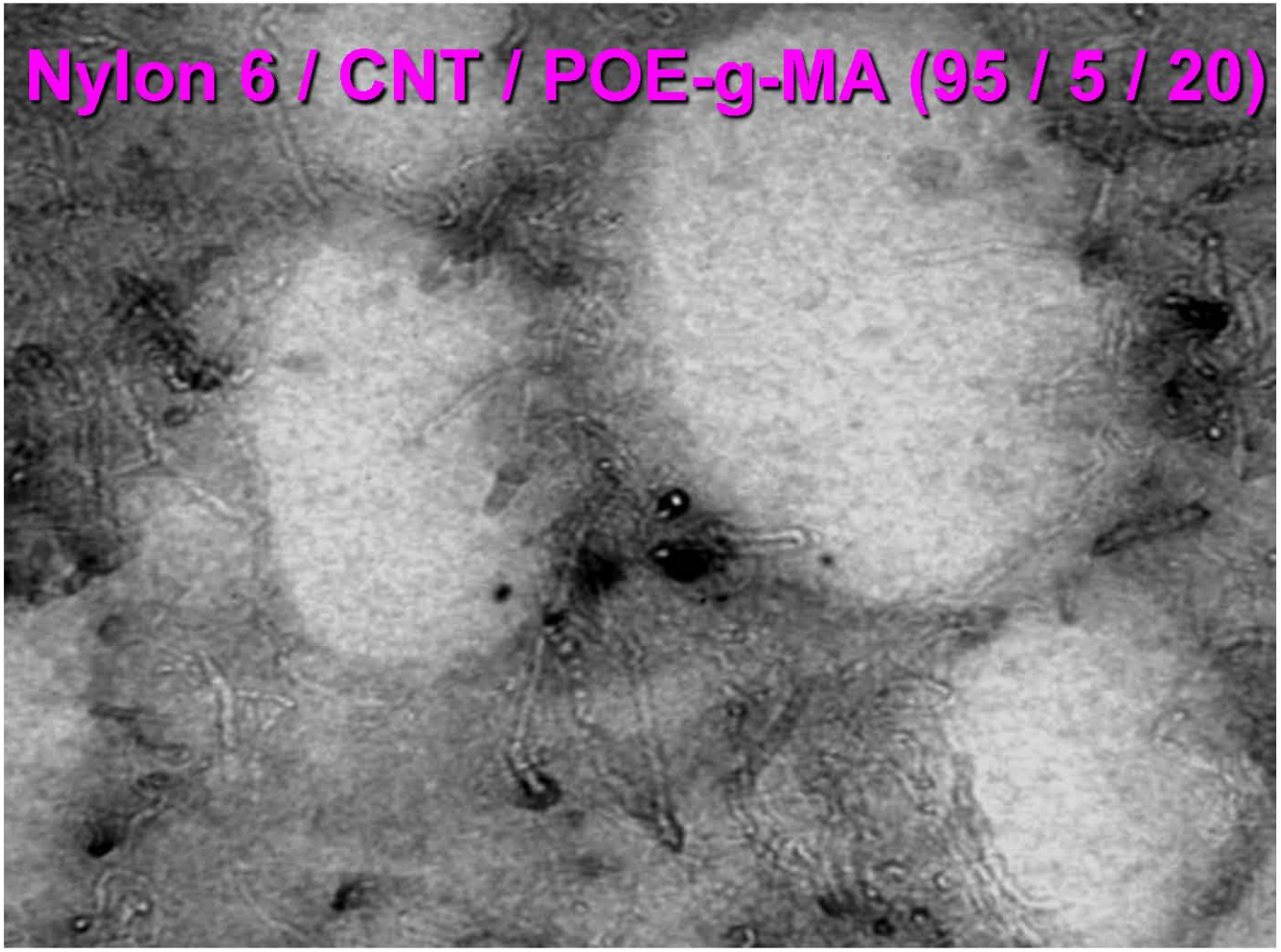


- **Conducting Filler: MWCNT**

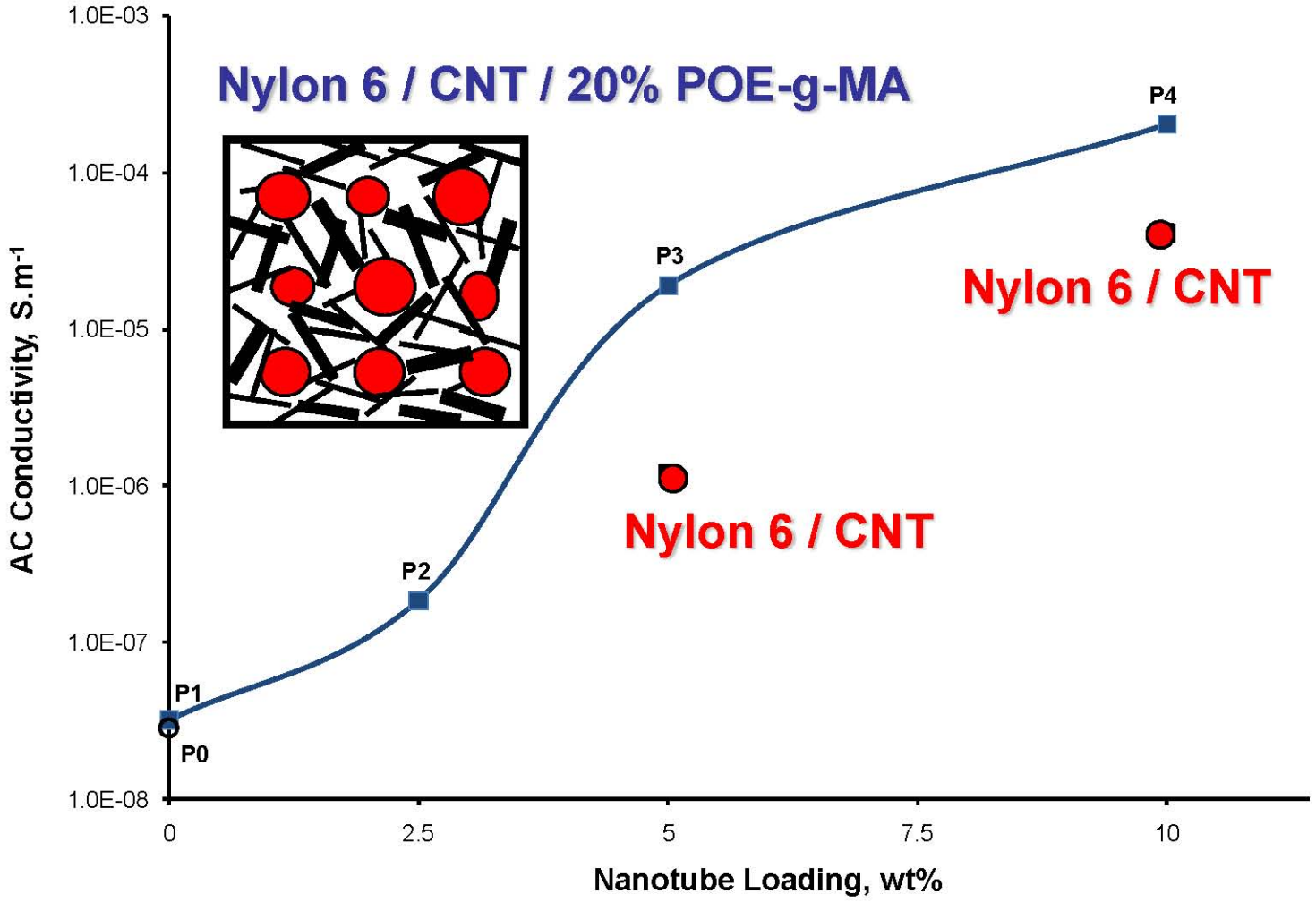
Dispersion of CNT in Nylon 6



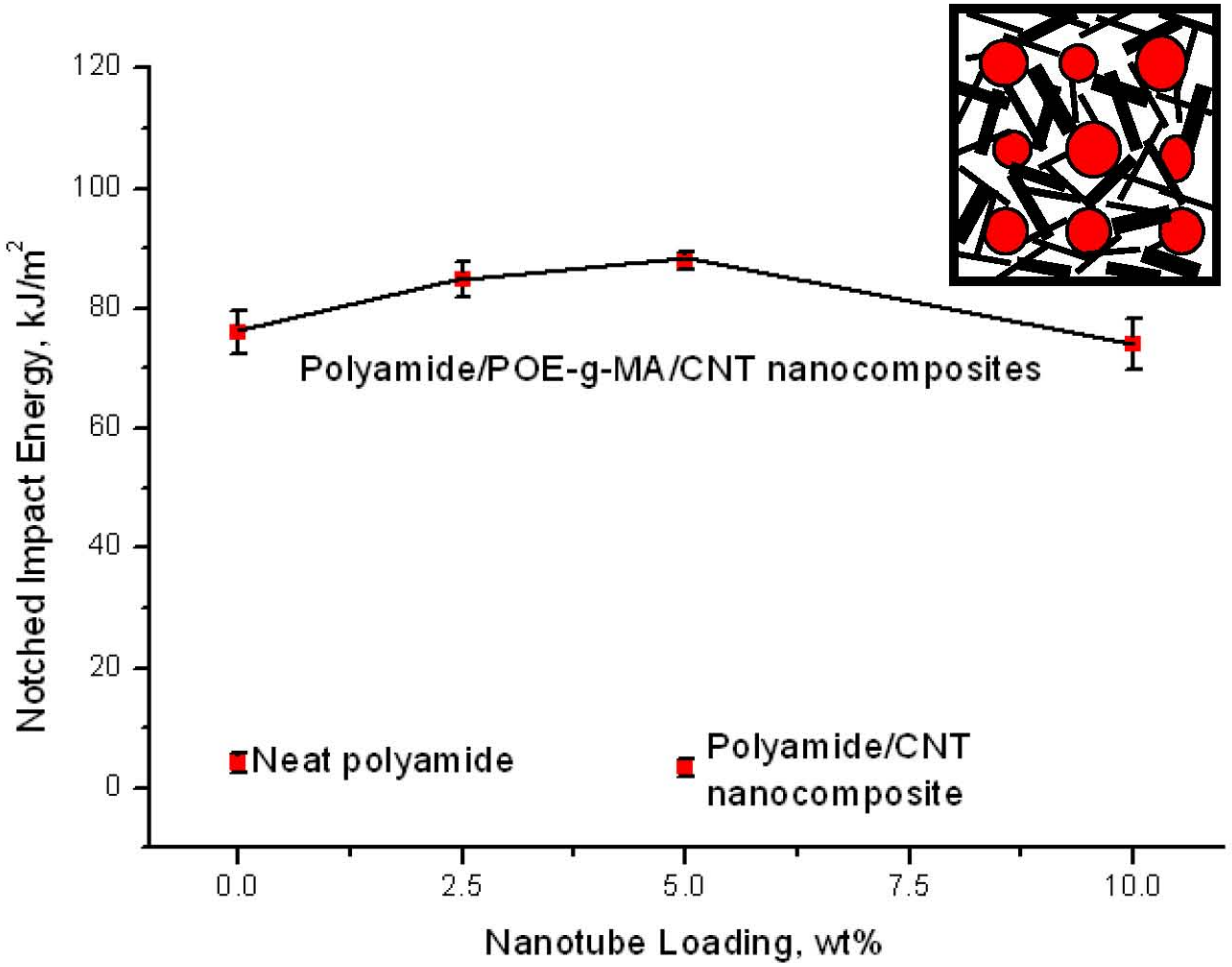
Selective Localization of CNT



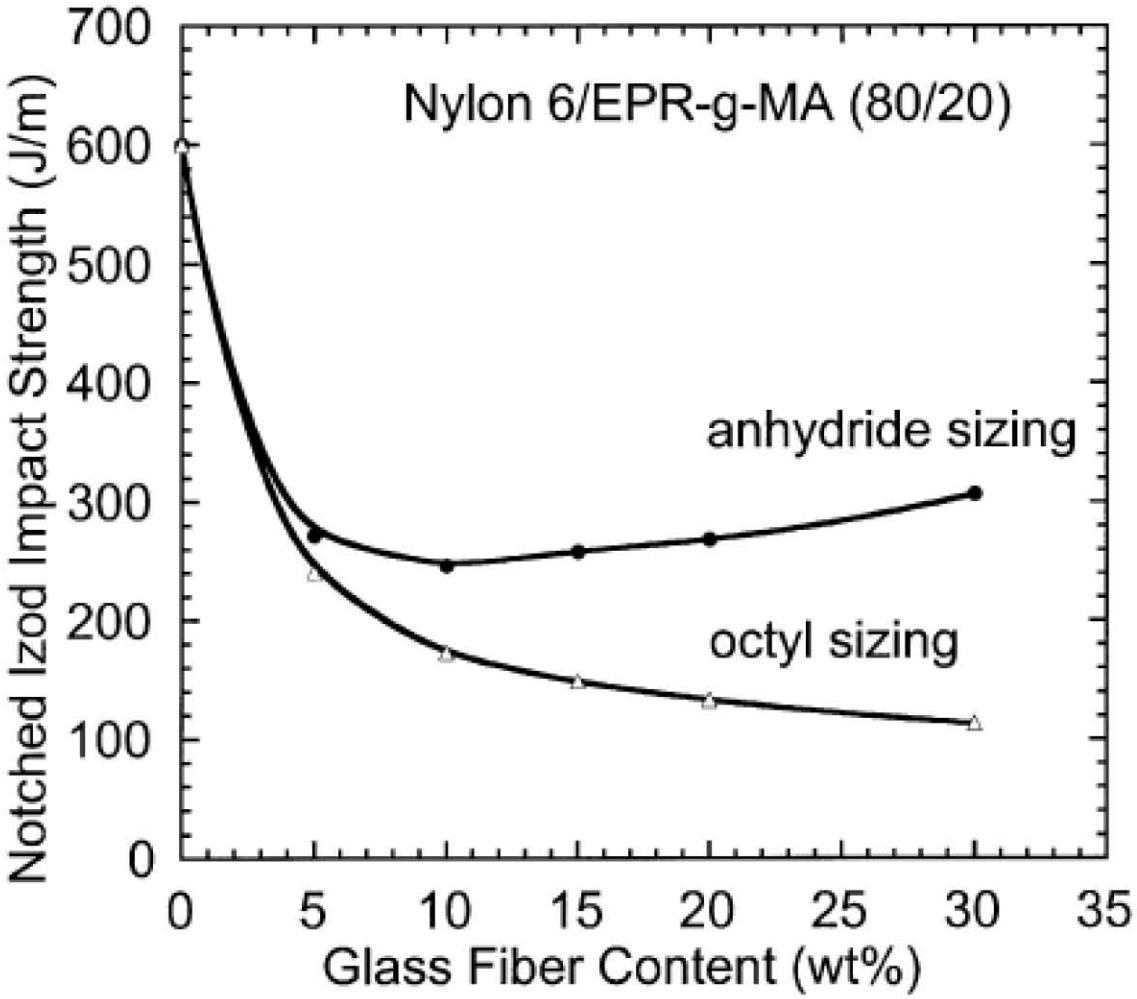
Volume Exclusion Effect



Toughening Efficiency of POE-g-MA



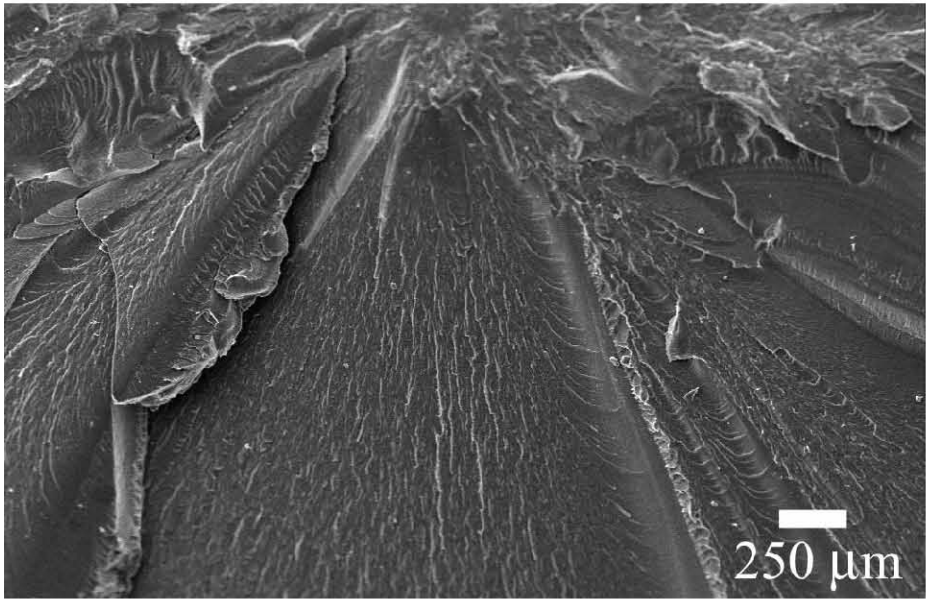
Detrimental Effect of GF on Toughness



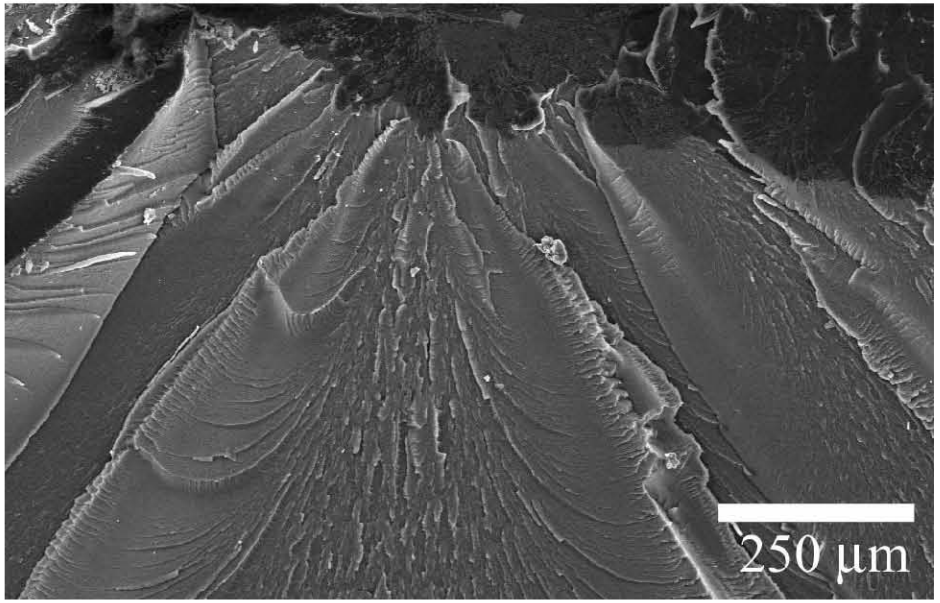
Paul DR, et al. Polymer, 2001, 43, 4673

Fracture Surfaces

Nylon 6

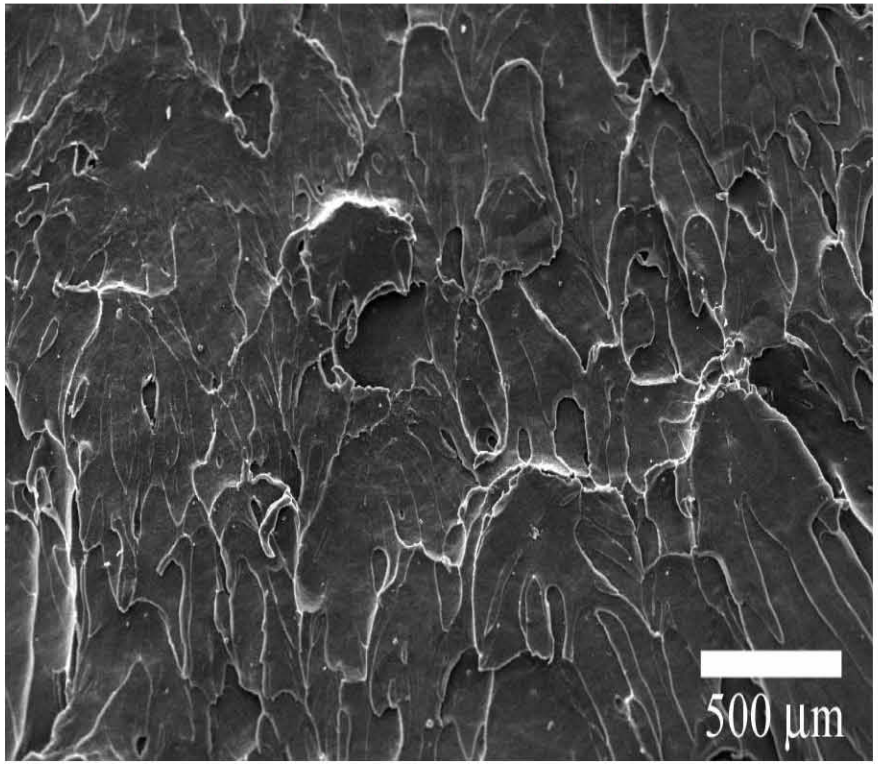


Nylon 6 / CNT (95 / 5)

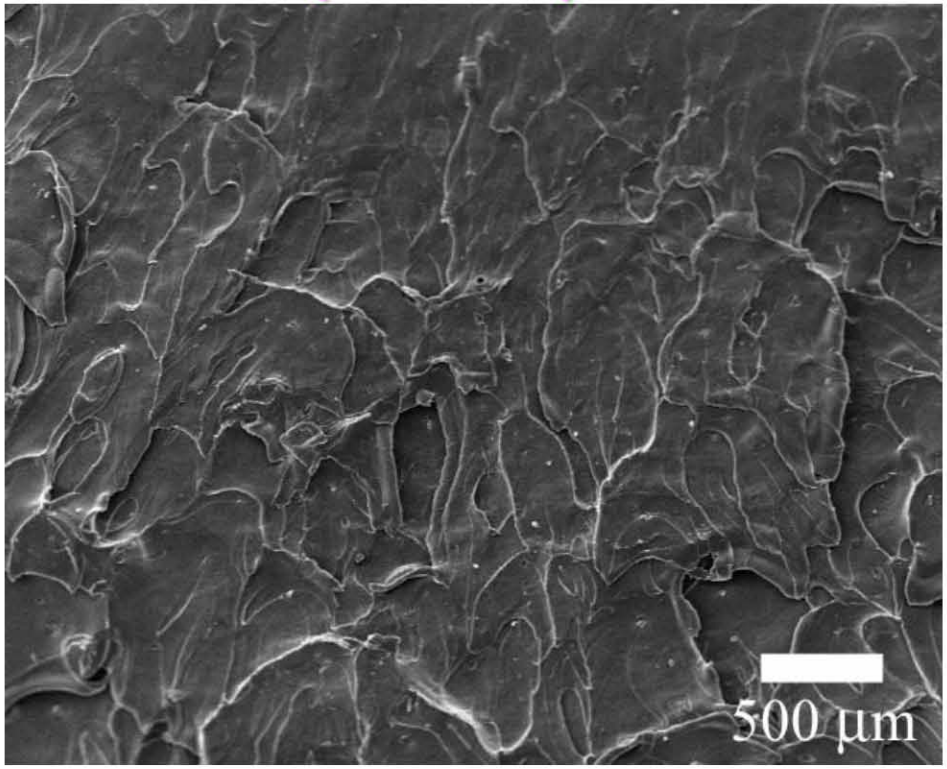


Fracture Surfaces

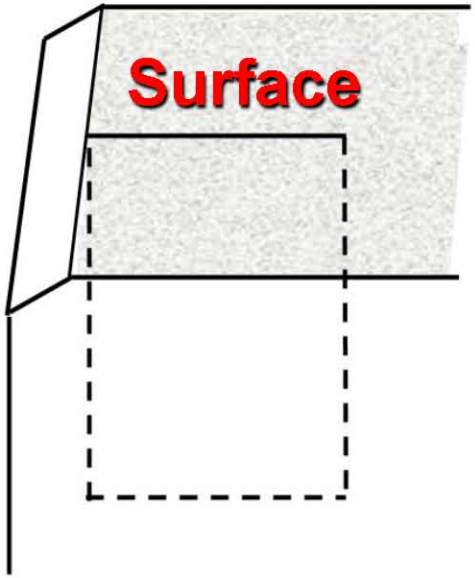
Nylon 6 / POE-g-MA / CNT (80 /15 / 5)



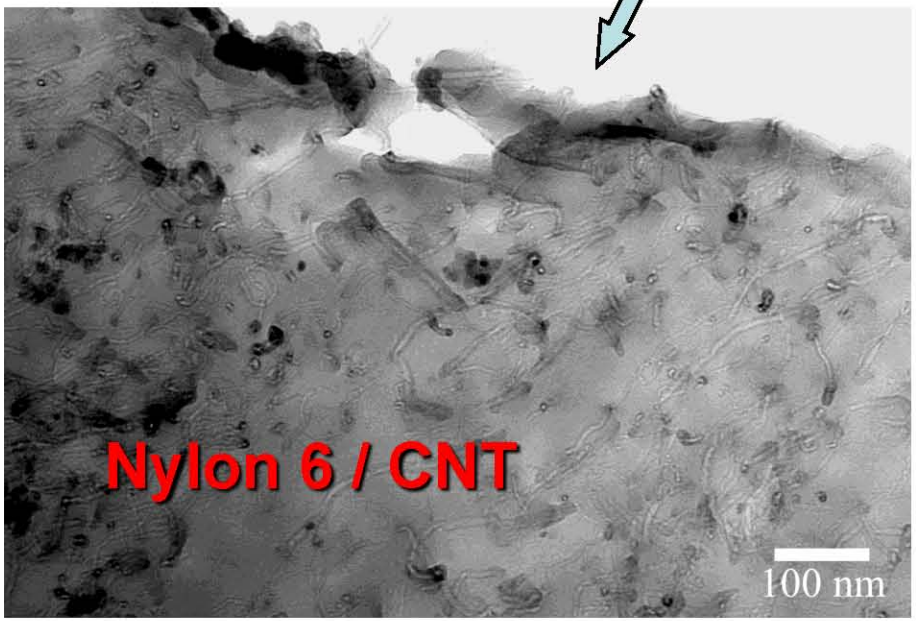
Nylon 6 / POE-g-MA (85 / 15)

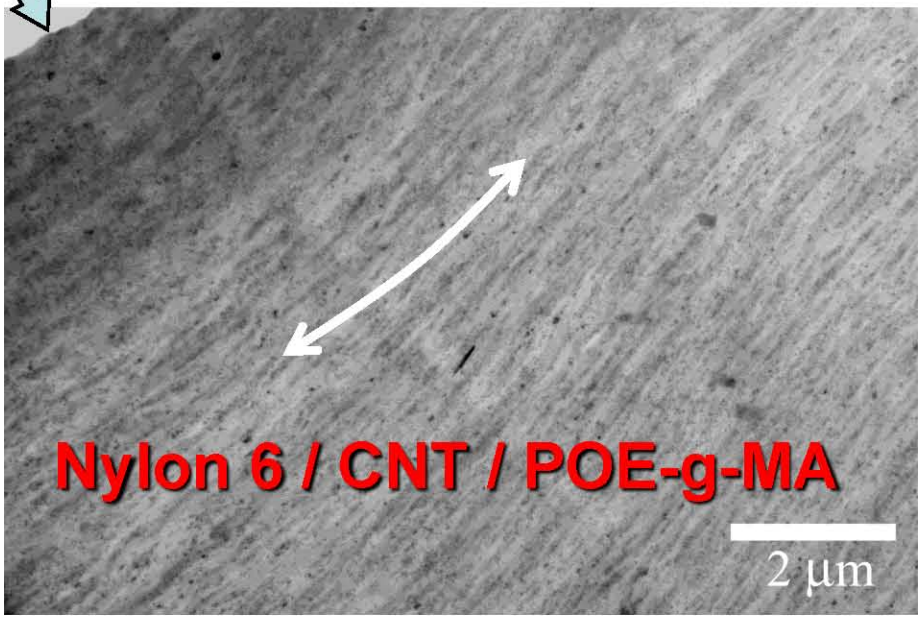


Sub-critically Deformed Zone



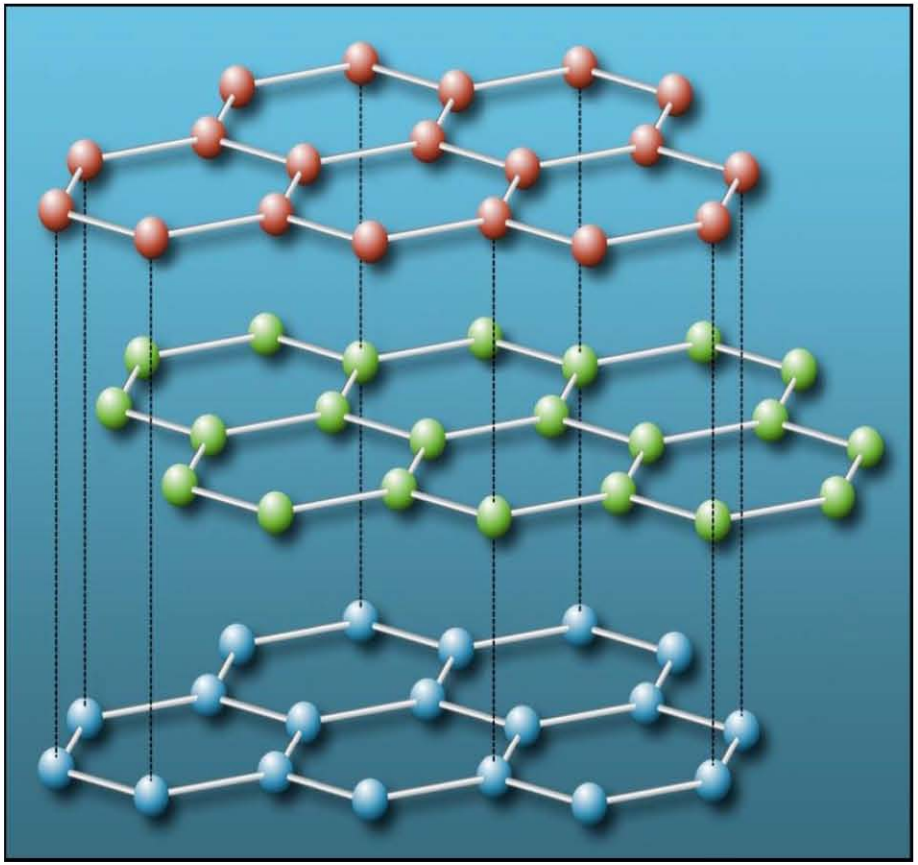
Fracture Surface





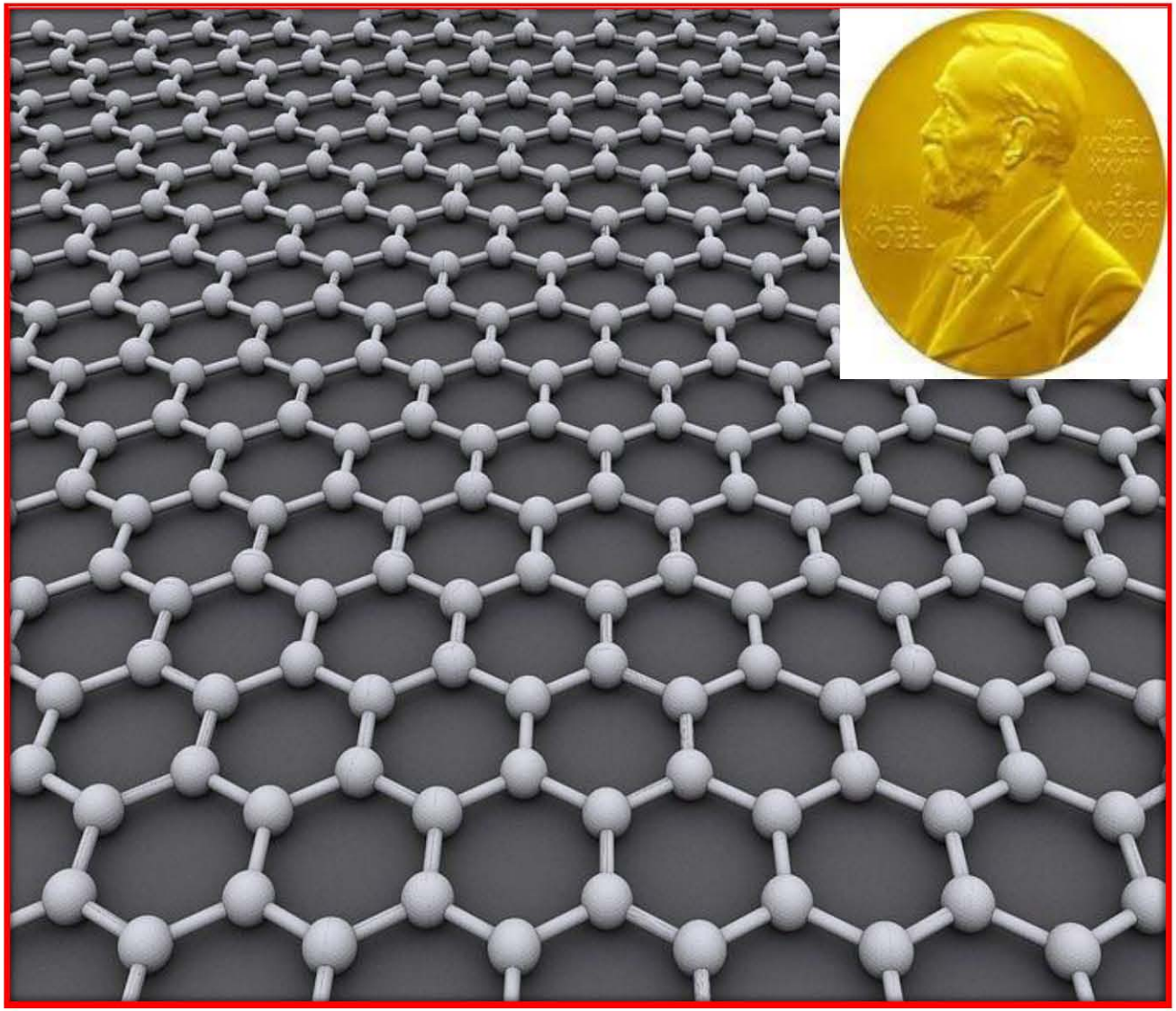
4.
Polymer / Graphene Nanocomposites

Graphene vs. Clay & CNT

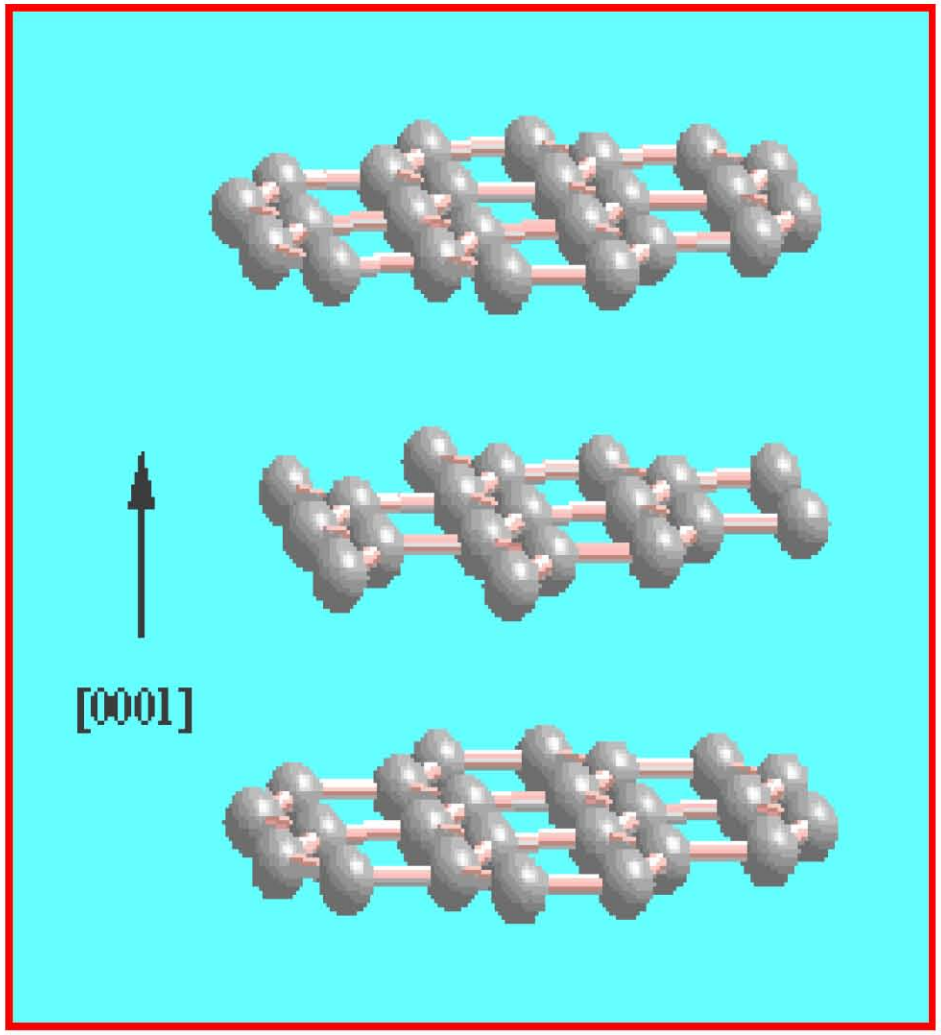


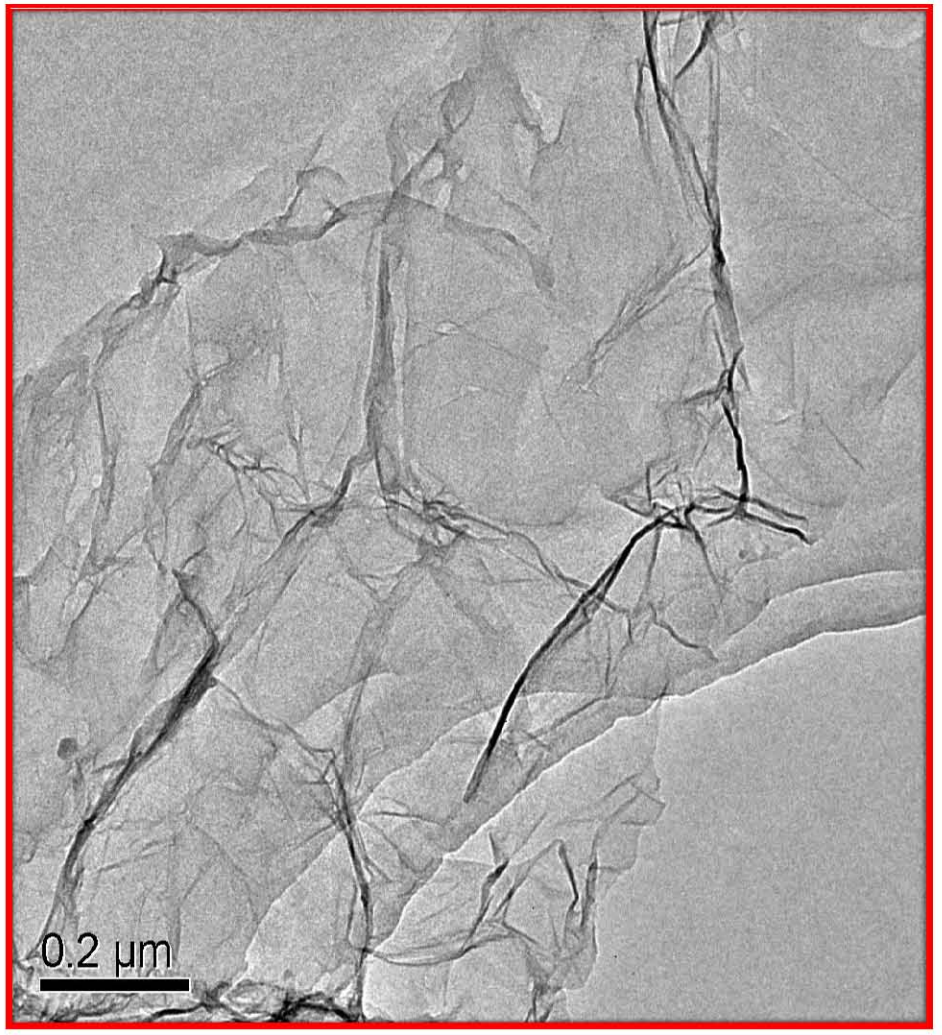
- Layered Structure
- High Aspect Ratio
- Superior Conductivities

Graphene

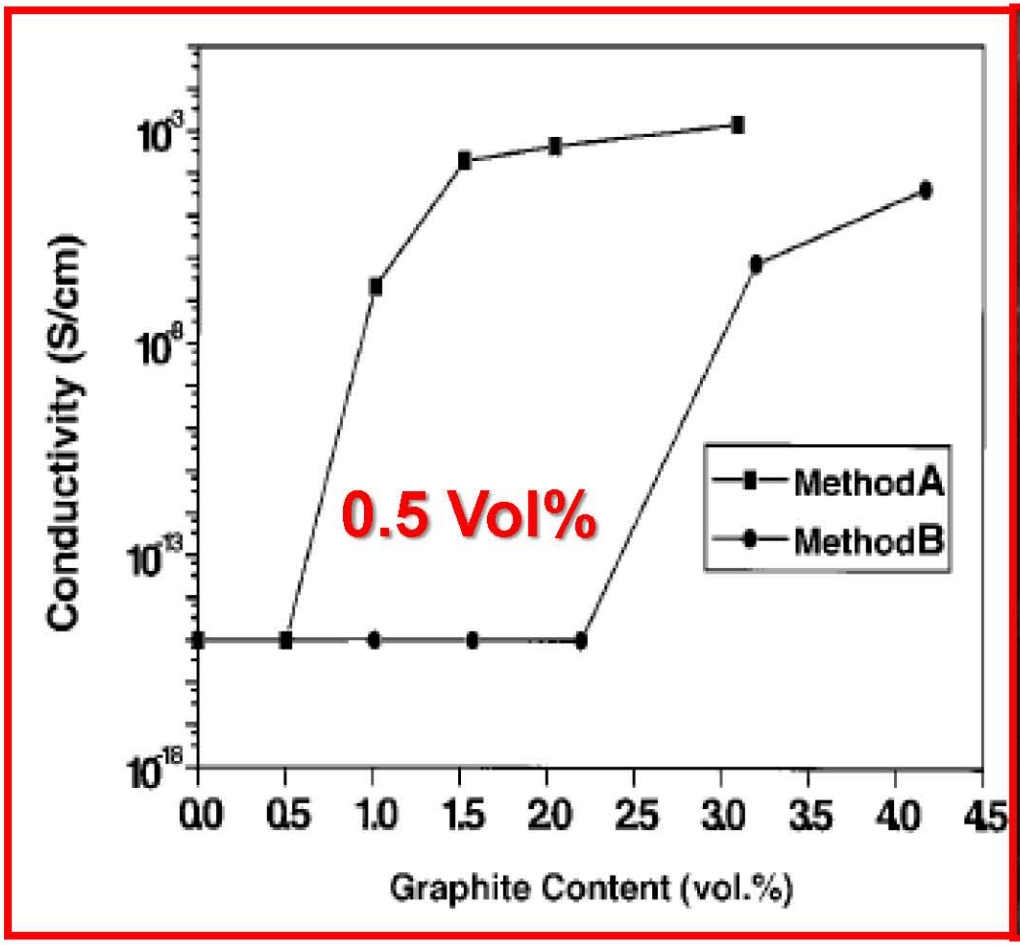


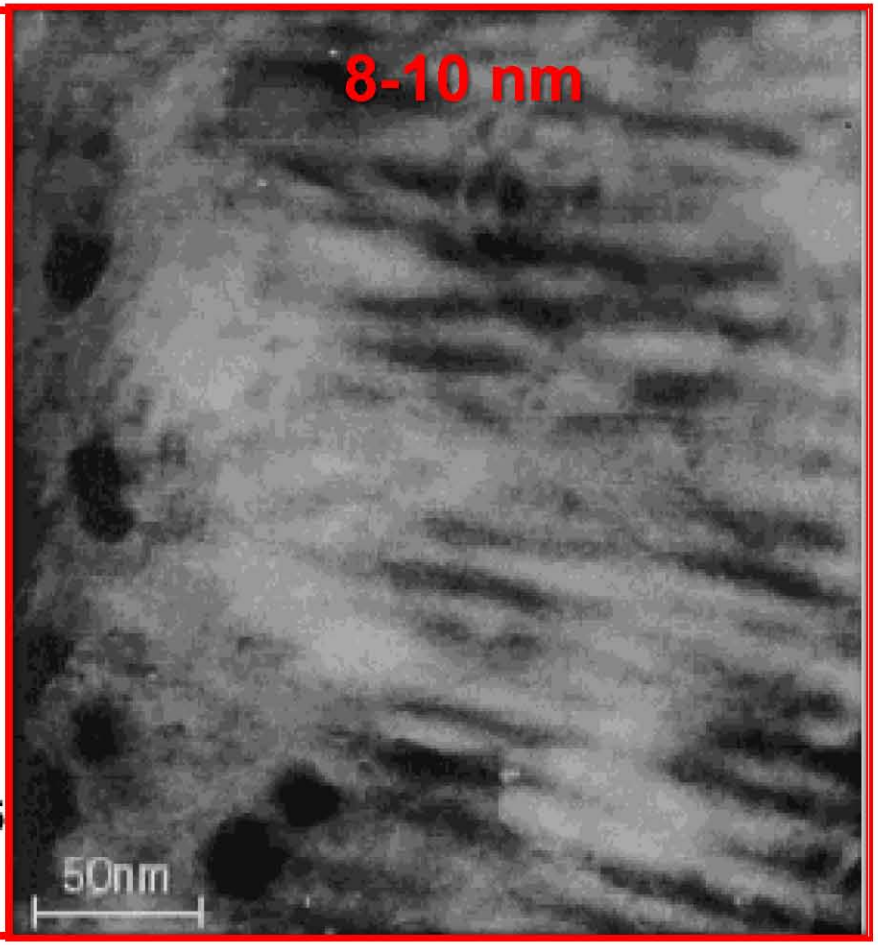
Graphene vs. Clay & CNT





Exfoliated Graphite/Nylon 6 Electrically Conductive Nanocomposites

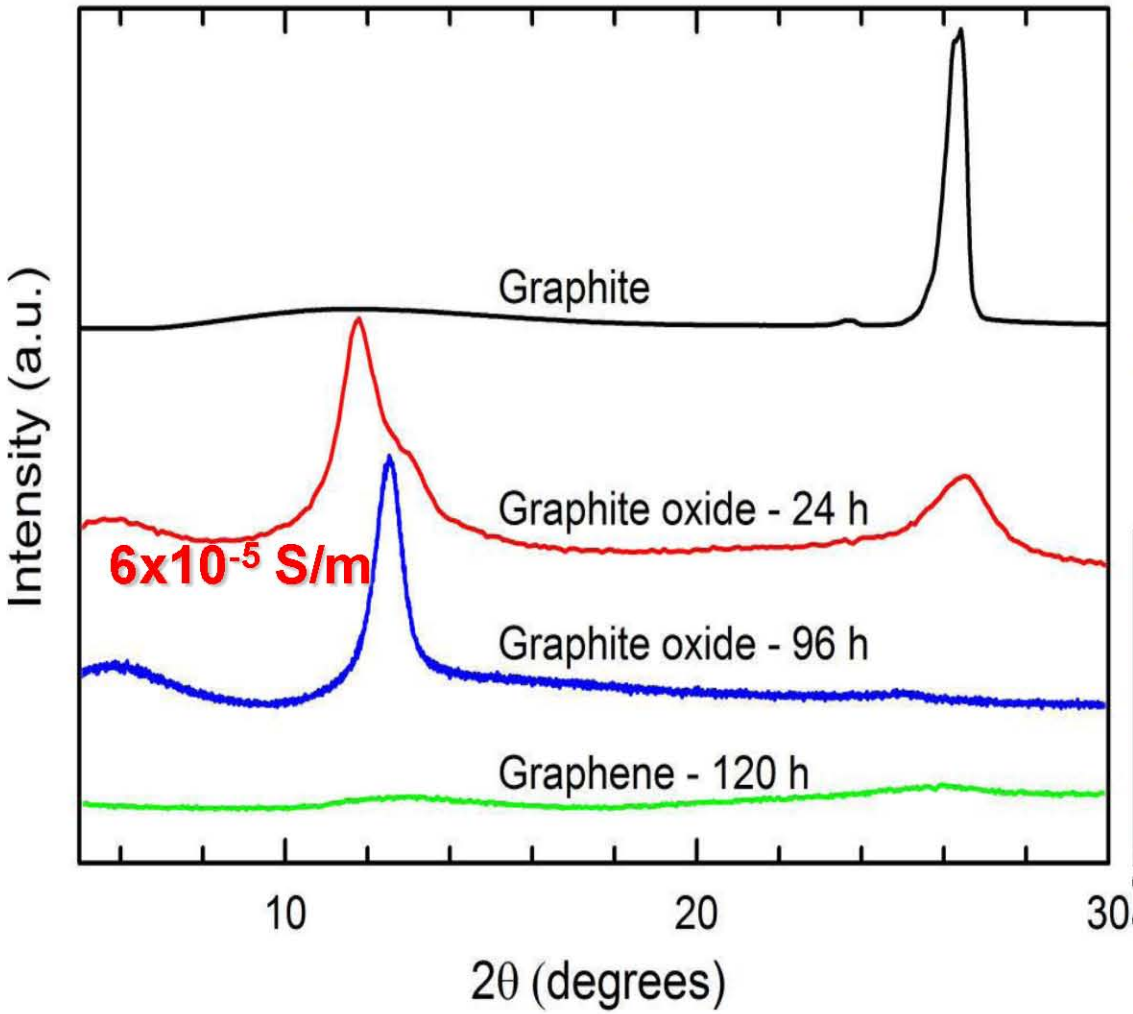




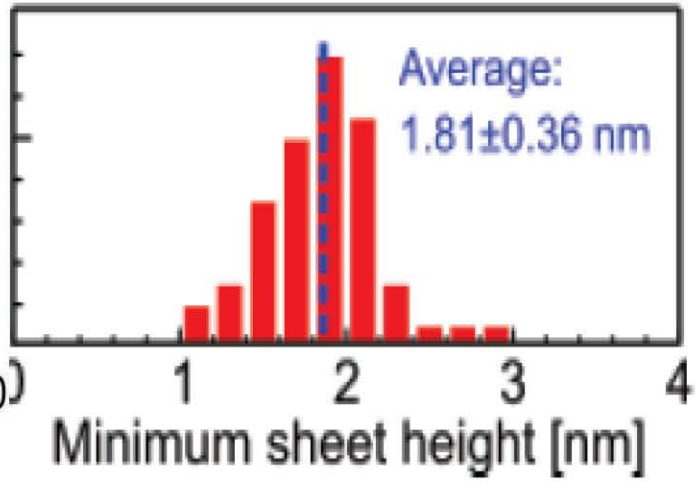
J. Polym. Sci., Part B Polym. Phys. 2000, 38, 1626

Chinese Patent ZL99108082.3 (2000)

(1) Thermal Exfoliation of Graphite Oxide

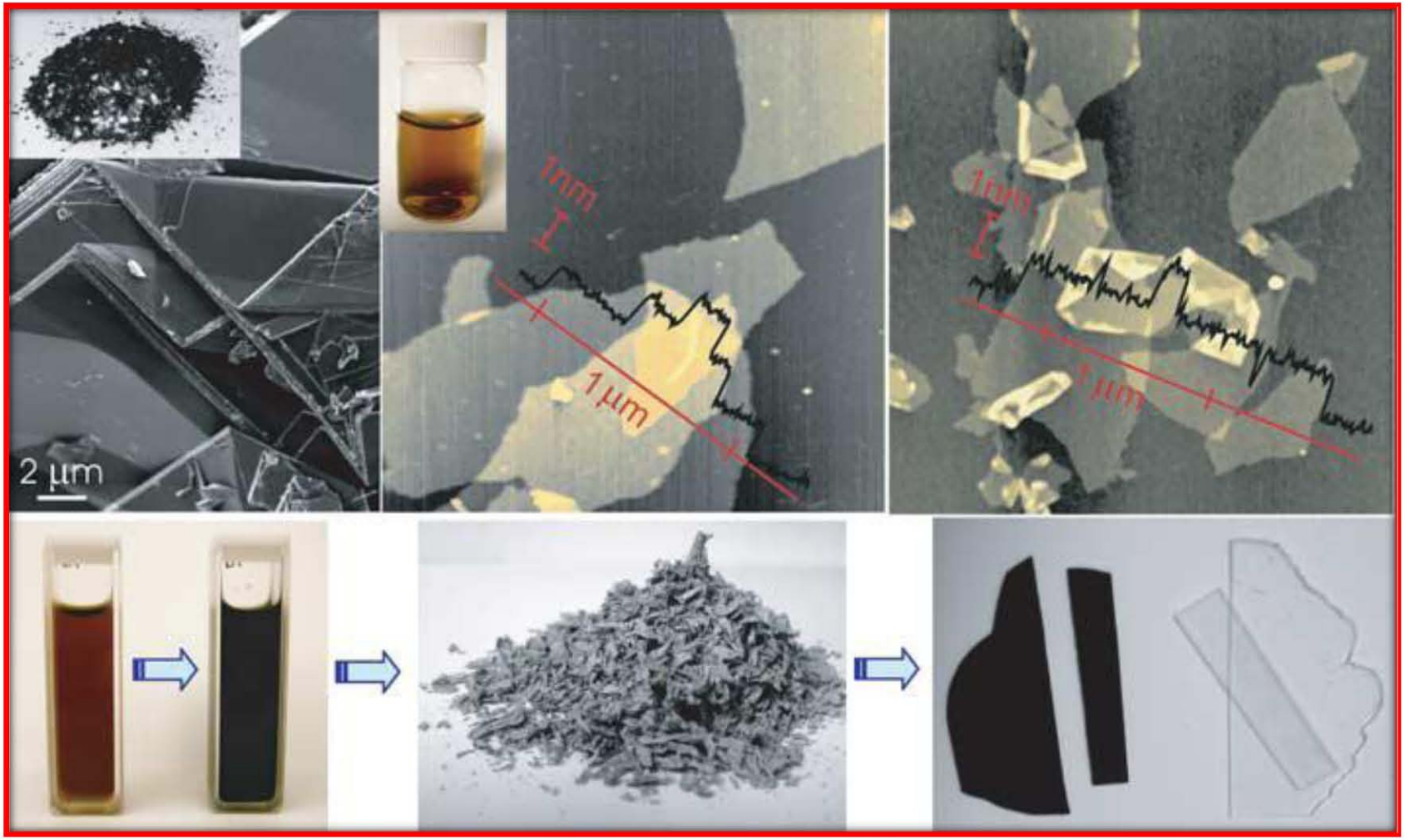


- Complete oxidation
- Pre-drying
- 1050 °C



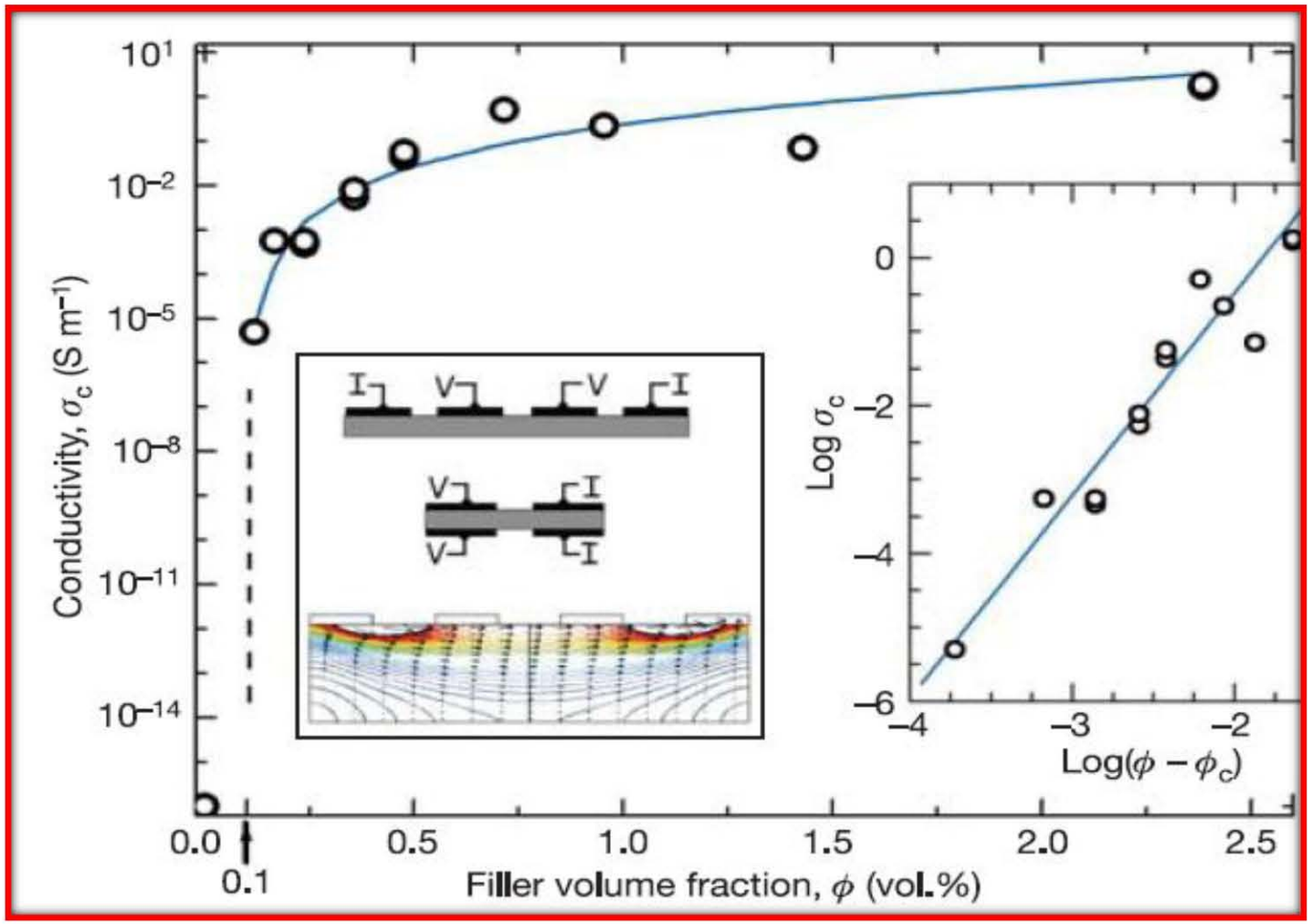
Aksay IA, et al. J. Phys. Chem. B 2006, 110, 8535

(2) Ultrasonication and Chemical Reduction of Graphite Oxide



Ruoff RS, et al. Nature 2006, 442, 282

Conductivre Polystyrene / Graphene Nanocomposites by Solution Mixing



Ruoff RS, et al. Nature 2006, 442, 282

Some Issues

Thermal Exfoliation

1050°C

750 m^2/g

Prof. Aksay JPC B 2006

Ultrasonication + Pre-modification + Reduction

Prof. Ruoff Nature 2006

- Thermal Exfoliation: Muffle Furnace, High T
- Ultrasonication: Pre-modification + Reduction
- Application in Polymers: Good dispersion

Our Recent Progress

1. Surface Modification, Reduction, and Dispersion

(1) Simultaneous Surface Functionalization and Reduction of Graphene Oxide with ODA

(2) Simultaneous Surface Functionalization and Reduction of Graphene Oxide with PPD

(3) Electrically Conductive Polyamide 6 / Graphene Oxide Nanocomposites by in-situ Reduction

(4) Electrically Conductive Phenolic Resin / Graphene Oxide Nanocomposites by in-situ Reduction

2. Conductive Nanocomposites with Less Graphene

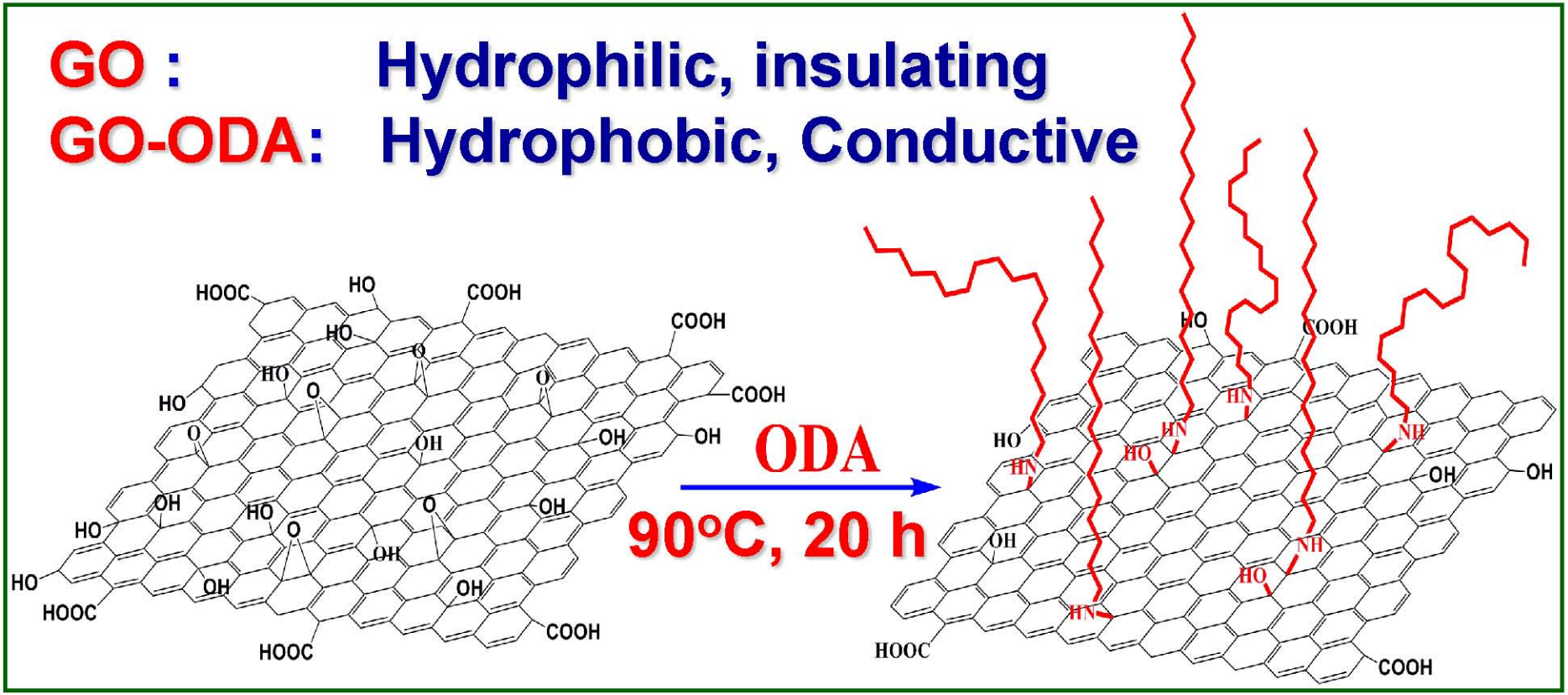
(5) Higher Electrical Conductivity of Polymers with Lower Content of Graphene

(6) Tough and Conductive Graphene-Polymer Microcellular Foams

(1) Simultaneous Functionalization and Reduction of Graphene Oxide with an Amine

GO : Hydrophilic, insulating

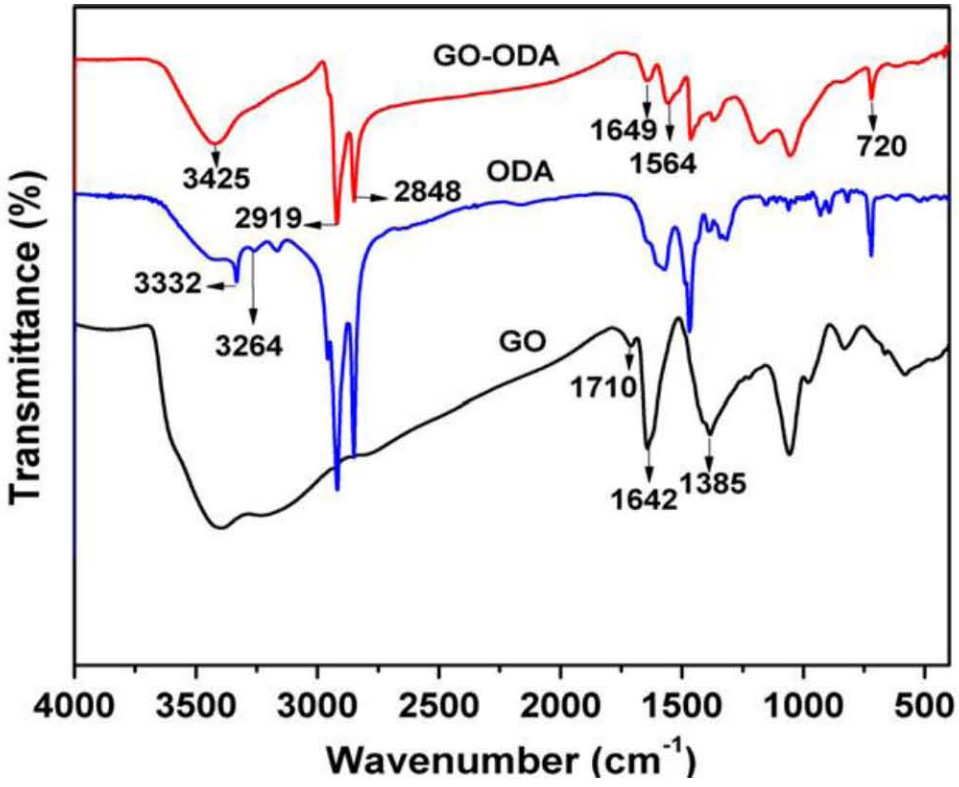
GO-ODA: Hydrophobic, Conductive



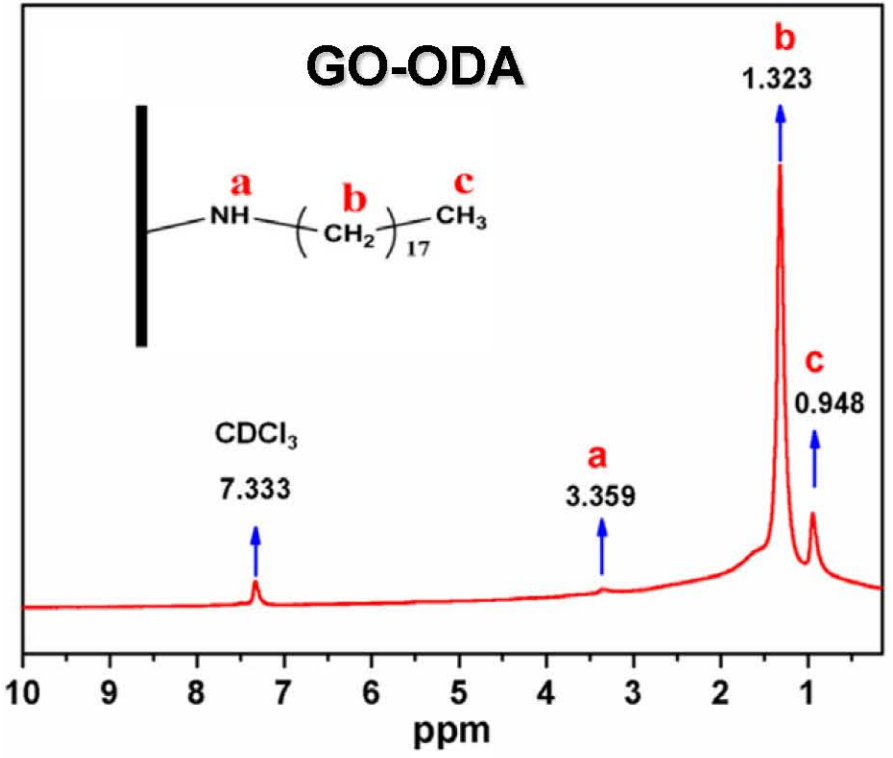
ODA: Octadecyl Amine

Simultaneous Surface Functionalization and Reduction of GO with ODA

Grafting with Octadecyl Chains



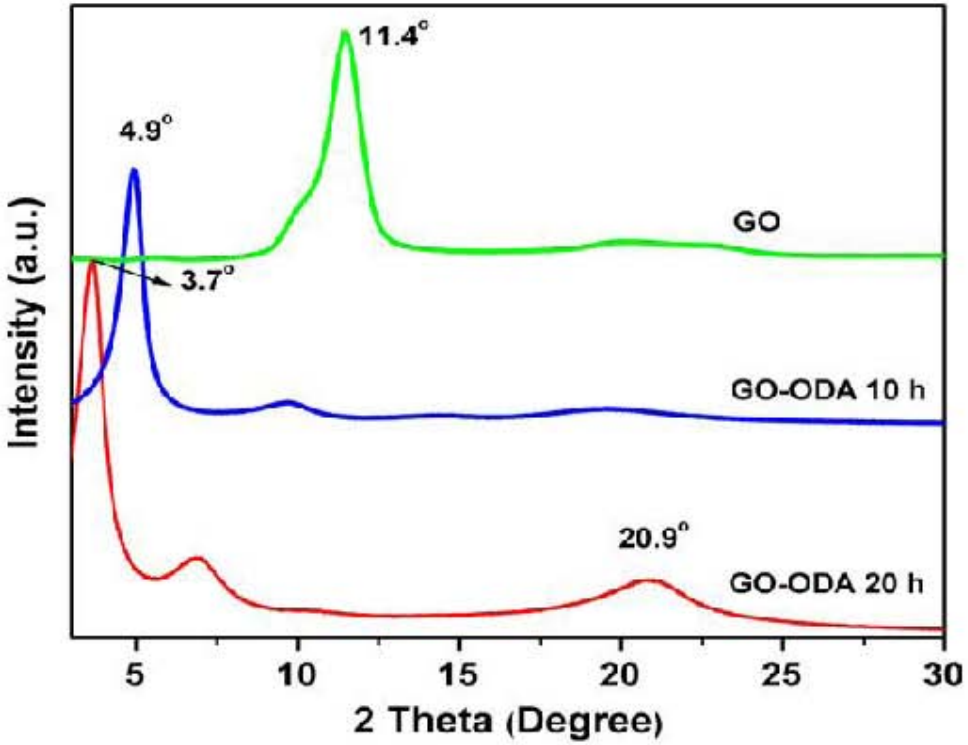
FT-IR



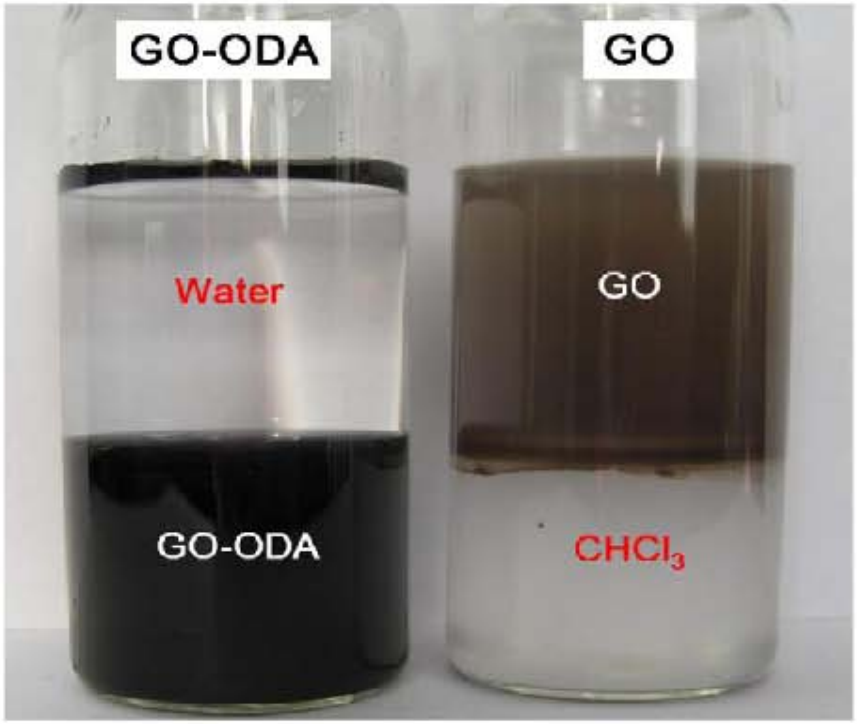
NMR

Simultaneous Surface Functionalization and Reduction of GO with ODA

Grafting with Octadecyl Chains



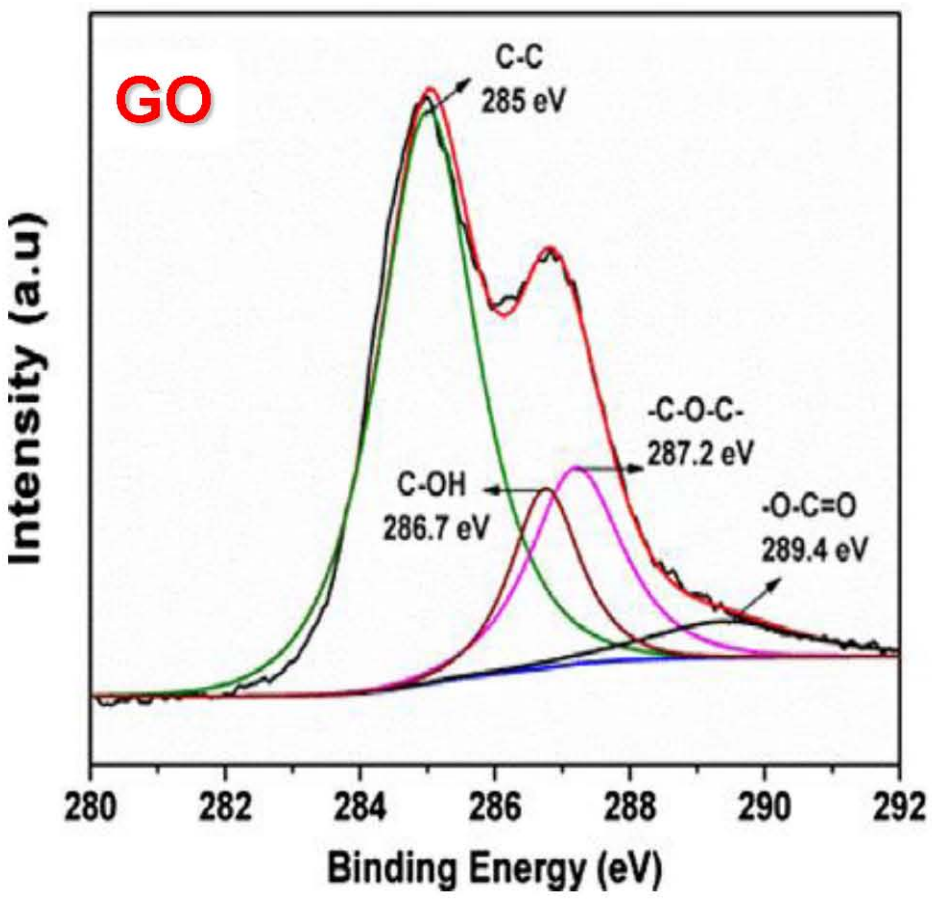
XRD

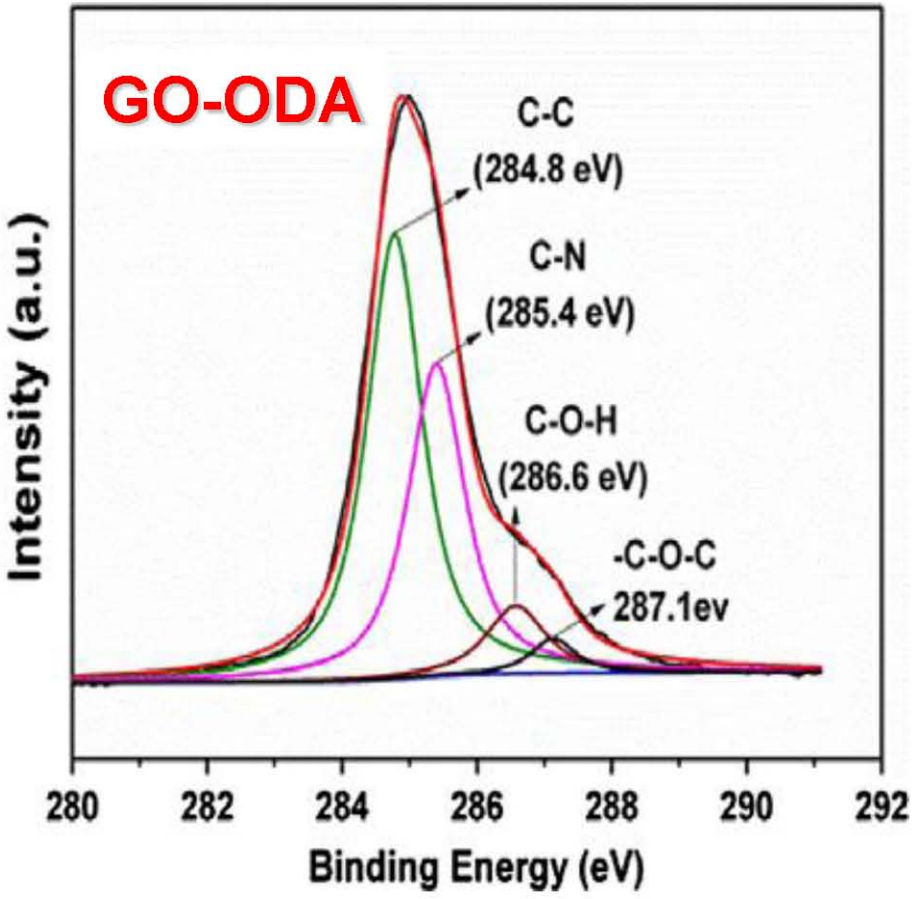


Selective Dispersion

Simultaneous Surface Functionalization and Reduction of GO with ODA

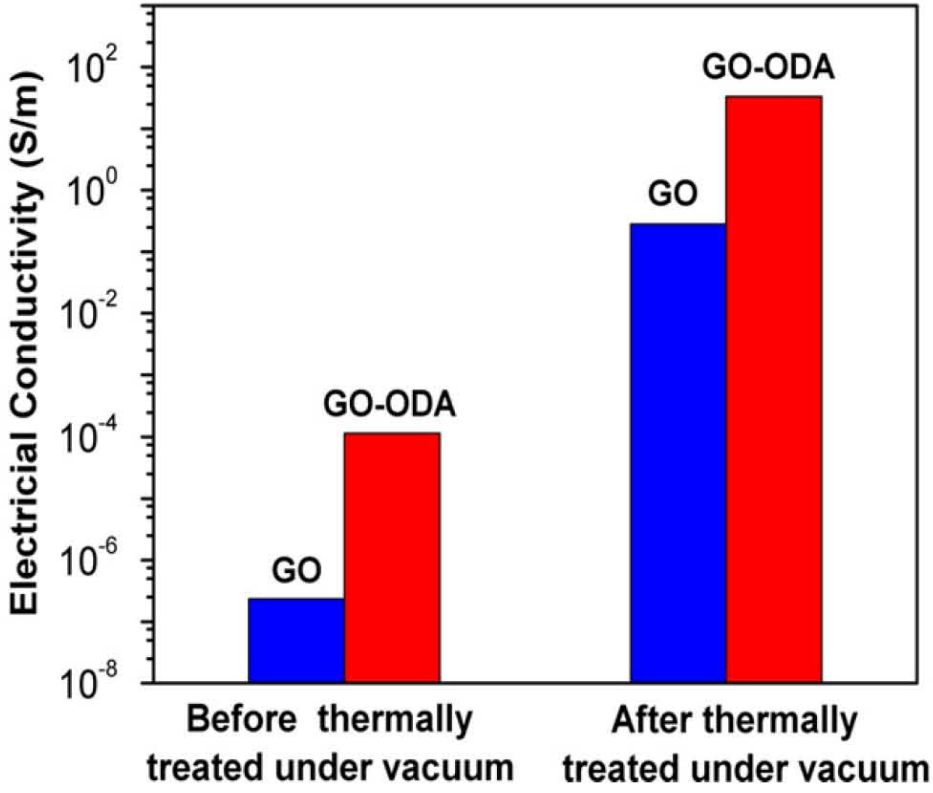
Reduction of GO during Refluxing (XPS)

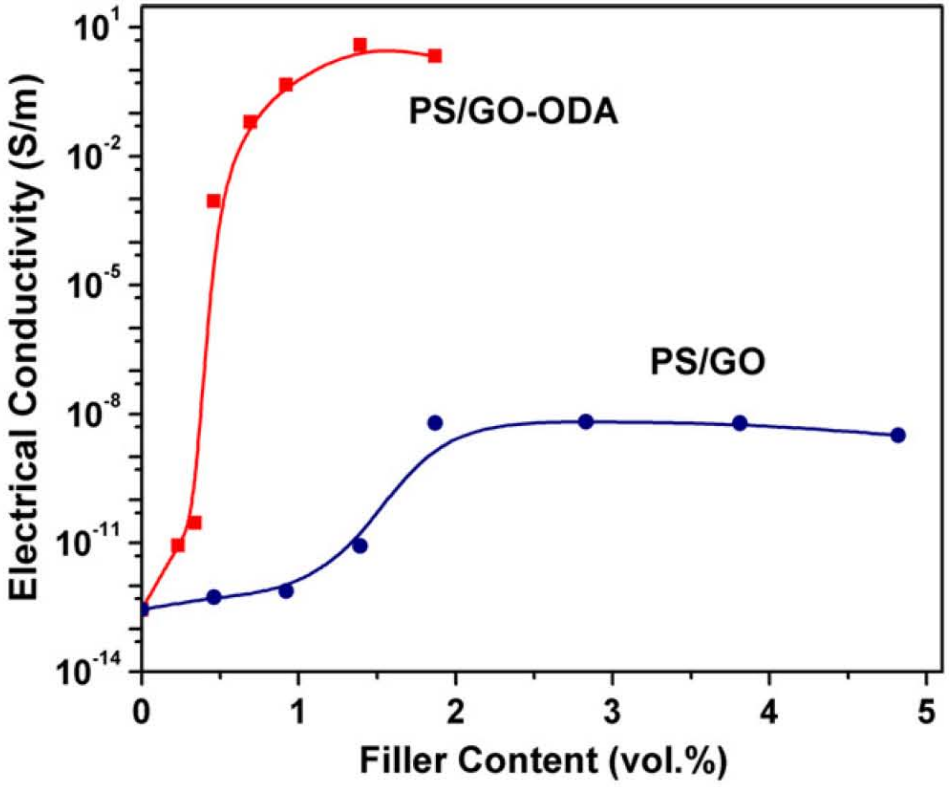




Simultaneous Surface Functionalization and Reduction of GO with ODA

- Reduction during Refluxing
- Incidental Thermal Reduction (210 °C, 25 min)

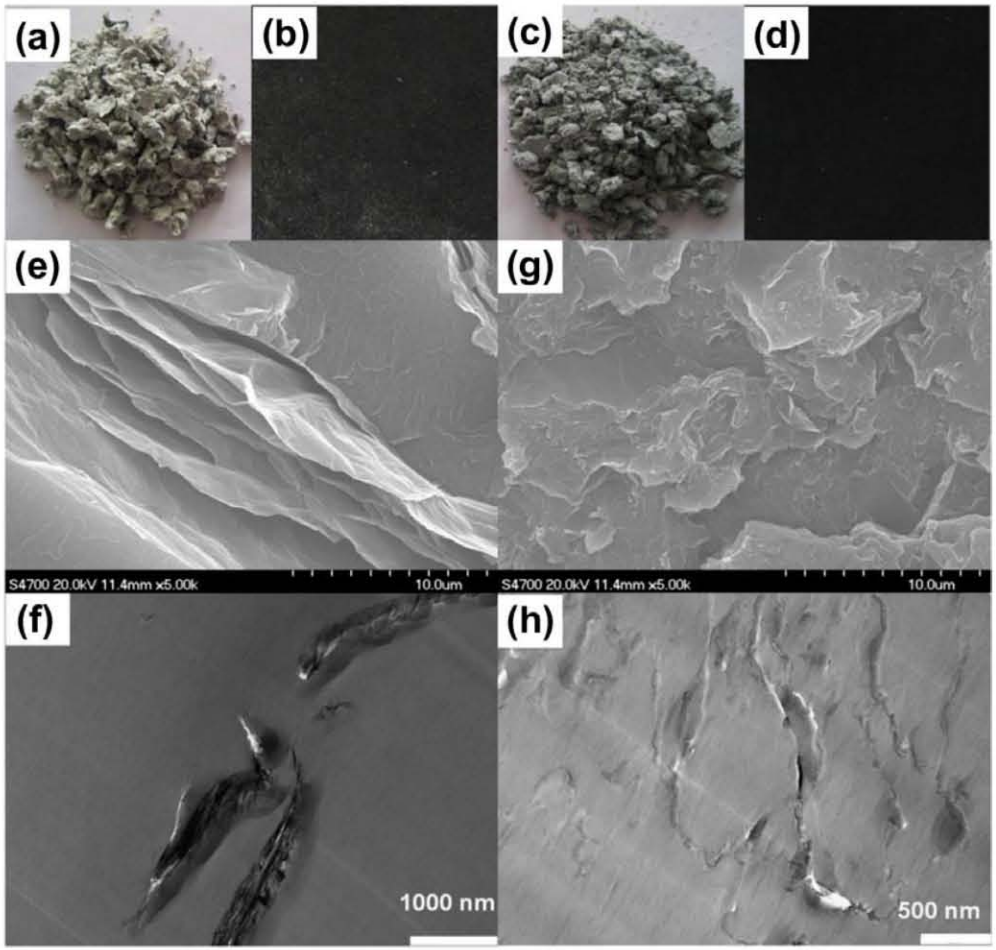




Electrical Conductivity Polystyrene Nanocomposites

Simultaneous Surface Functionalization and Reduction of GO with ODA

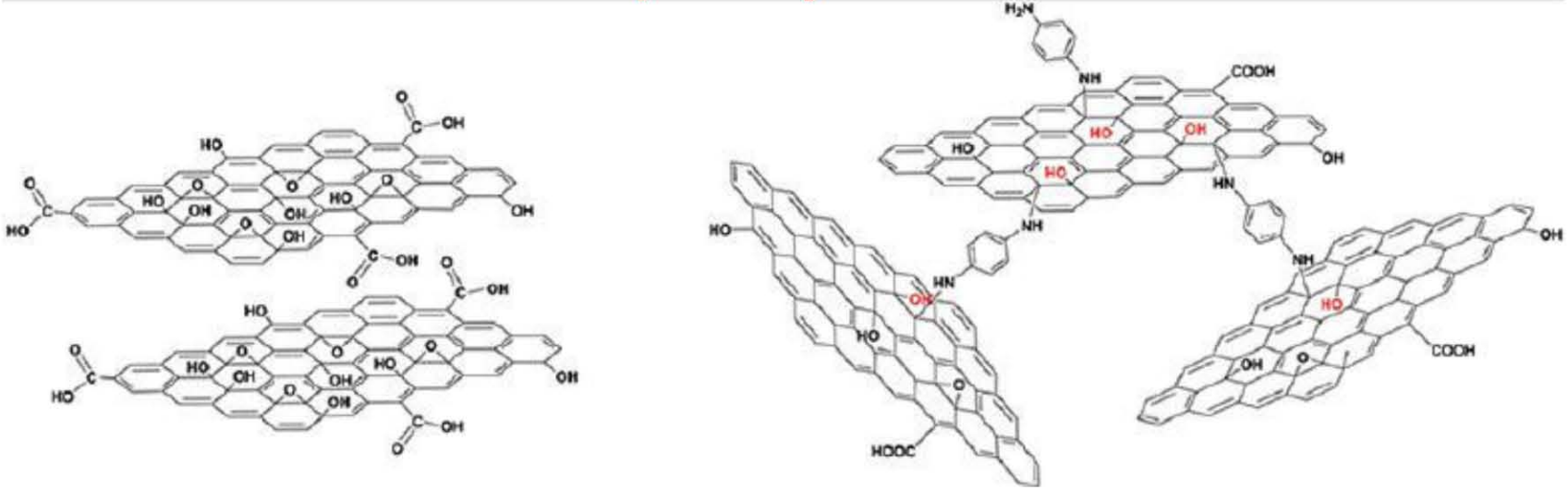
PS / GO PS / GO-ODA



- Improved dispersion by surface modification
- Reduction during refluxing with ODA
- Incidental thermal reduction during the compression moulding

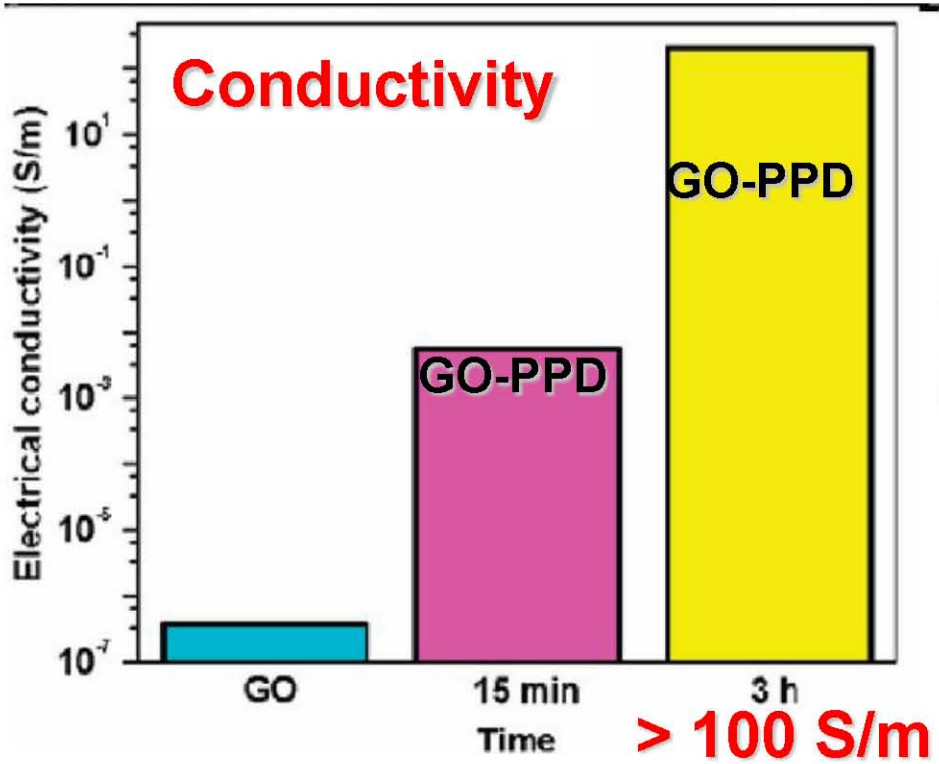
(2) Simultaneous Functionalization and Reduction of GO with p-Phenylene Diamine

PPD: p-Phenylene Diamine

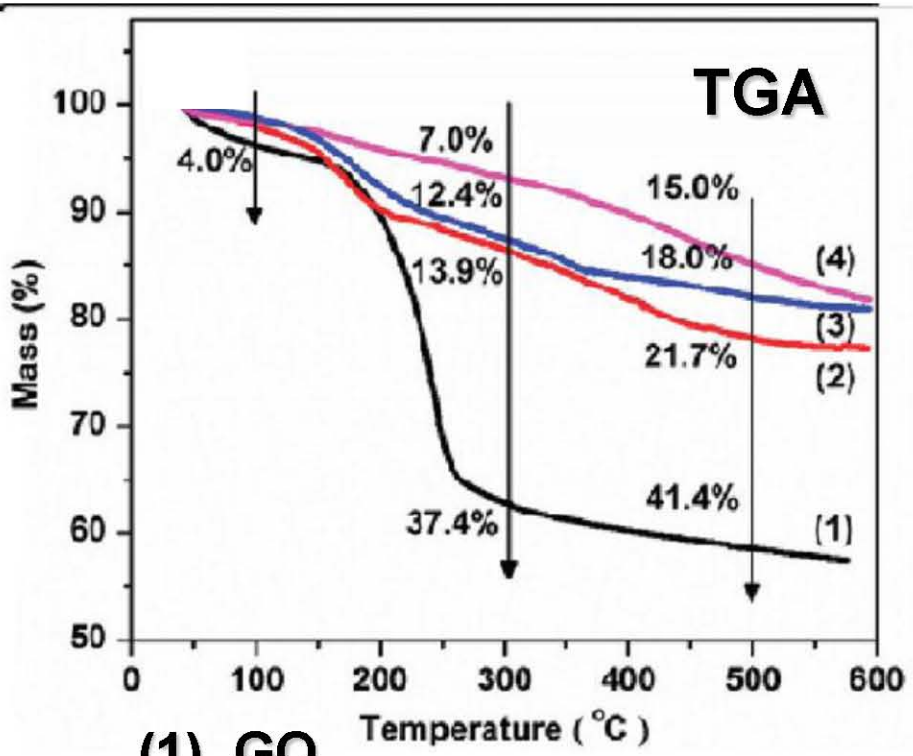


Simultaneous Surface Functionalization and Reduction of GO with PPD

Reduction



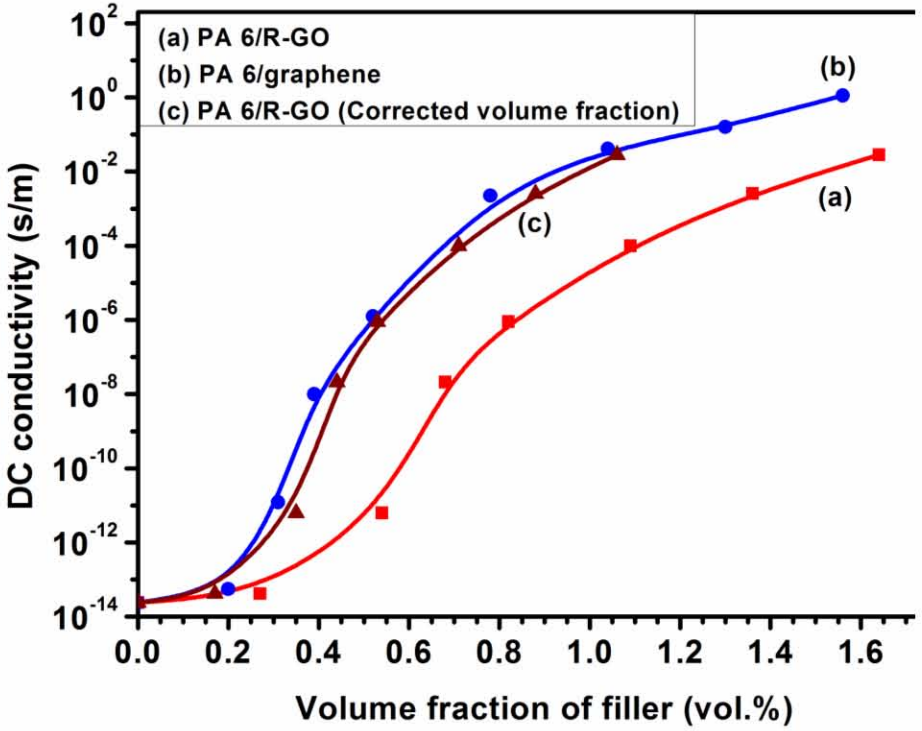
Contribution of Ammonia

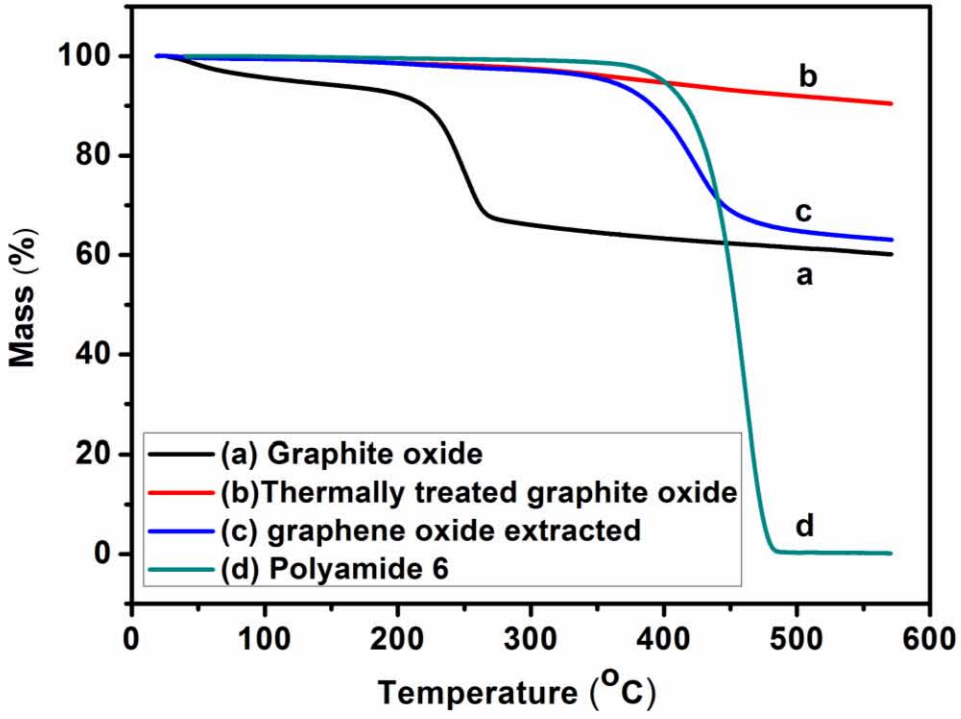


(1) GO
(2) GO-PPD-15 min
(3) GO-PPD-3 h without NH_3
(4) GO-PPD-3 h

(3) Electrically Conductive and Thermally Stable Polyamide 6 / GO Nanocomposites

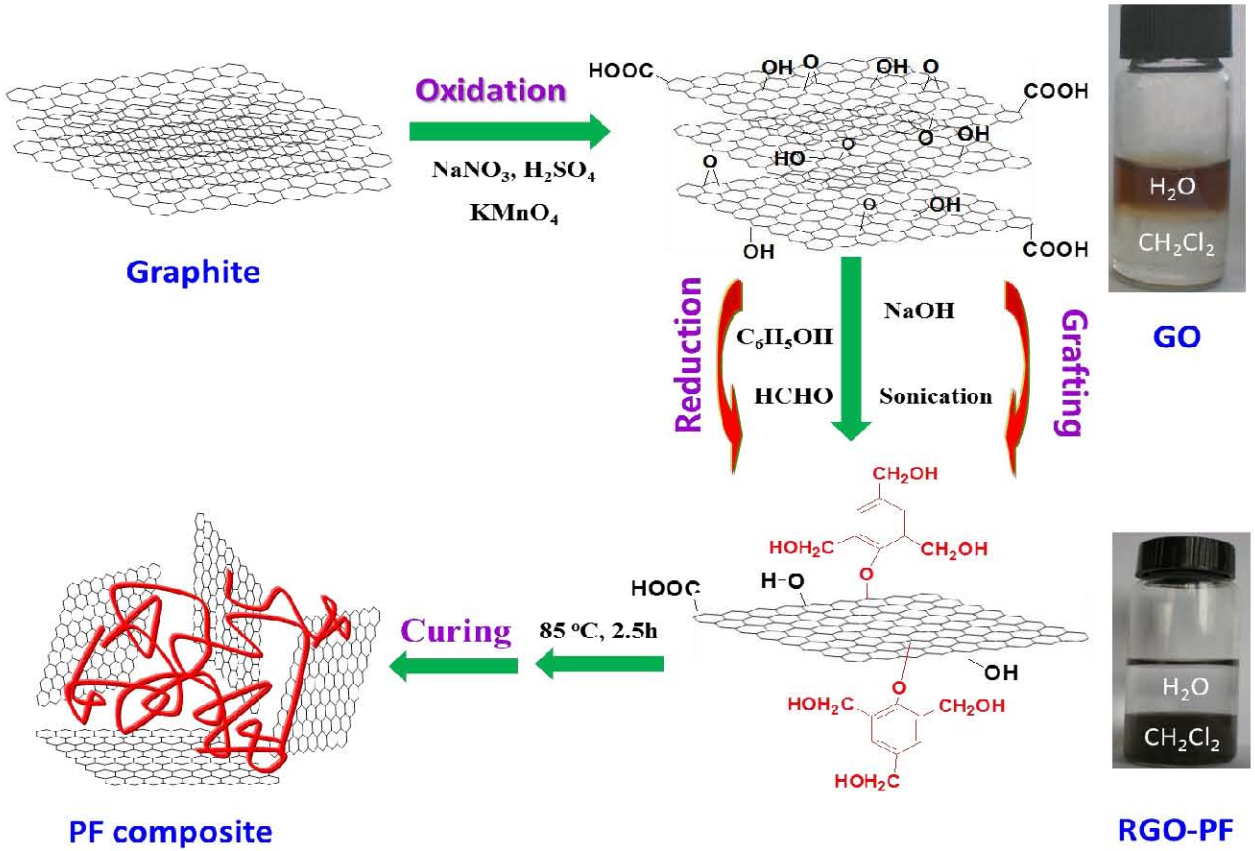
- In Situ Polymerization of ε-Caprolactam in the Presence of GO at 260 °C for 10 h
- In Situ Reduction of GO
- No Pre-Modification of GO





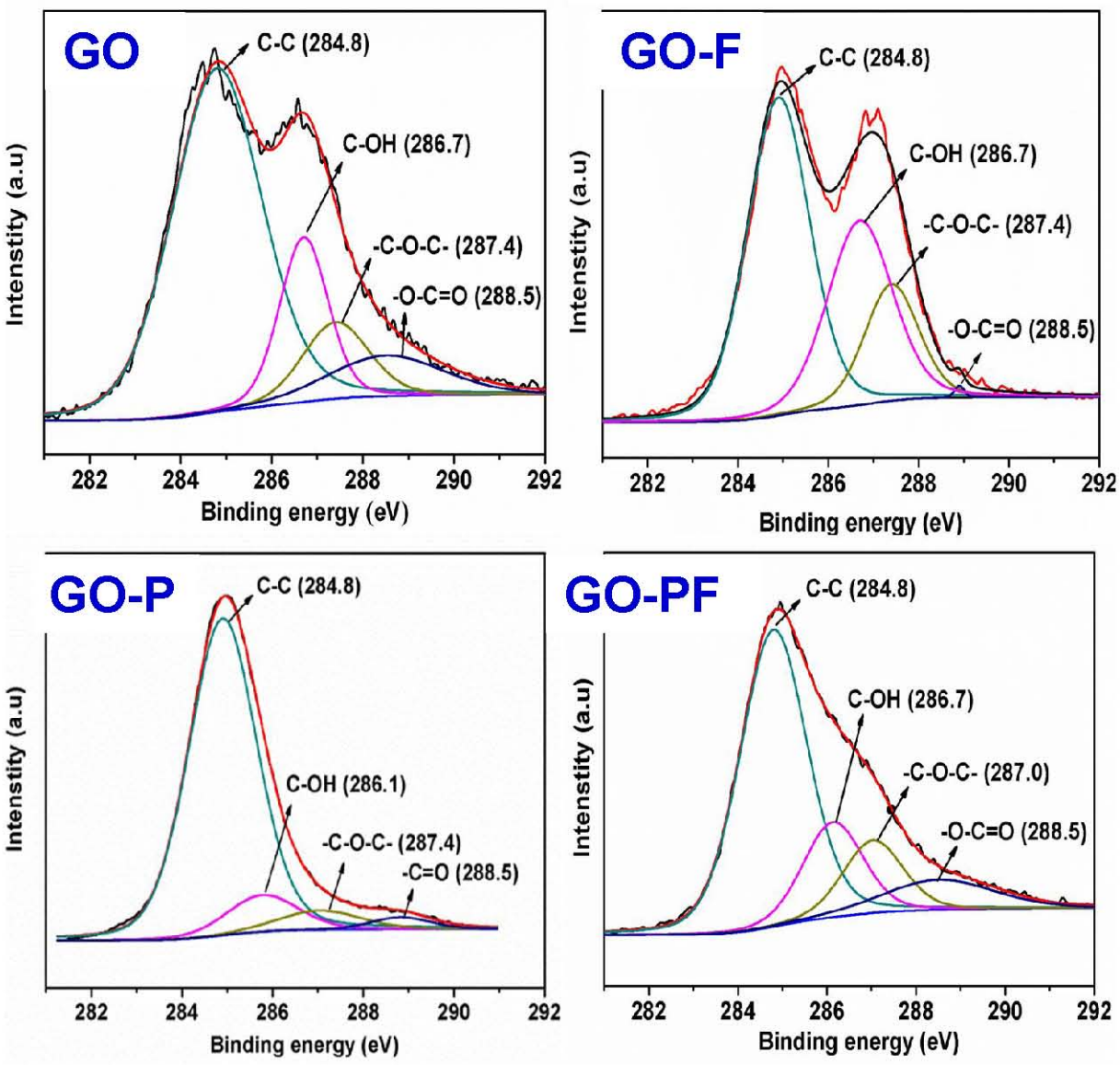
(4) Electrically Conductive Phenolic Resin / GO Nanocomposites by in-Situ Reduction

- GO was reduced and functionalized during the in situ polymerization
- GO was converted to graphene with phenol as main reducing agent



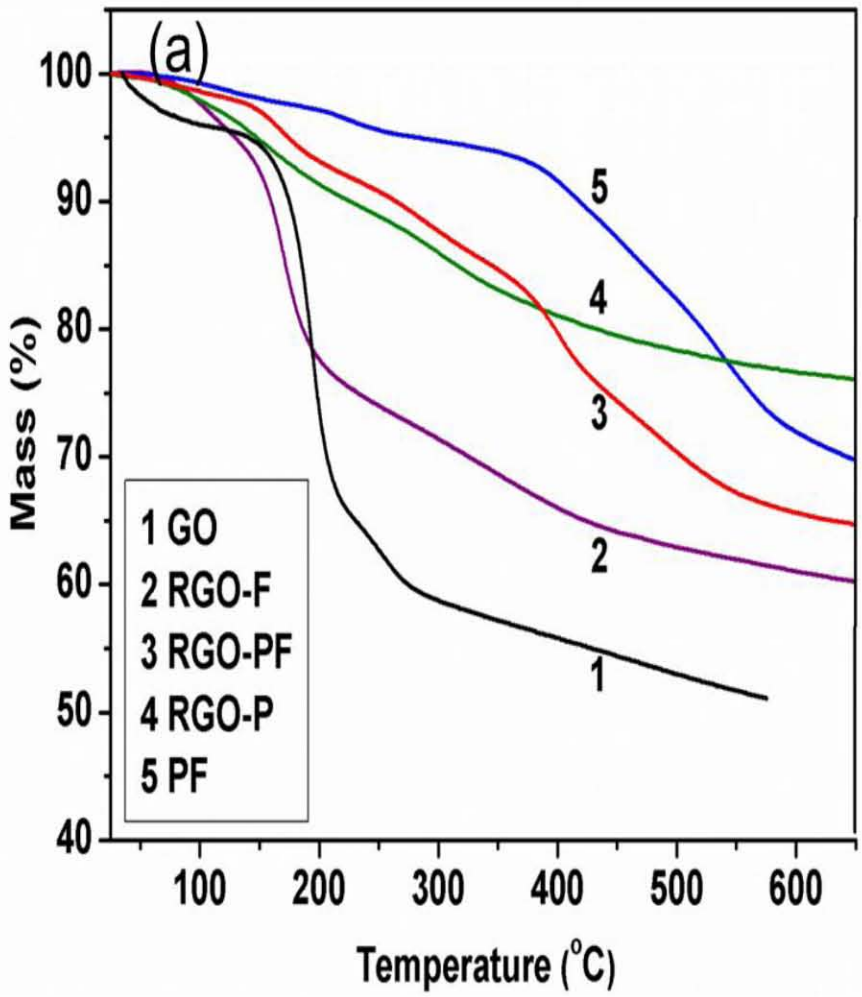
Reduction and Functionalization of GO

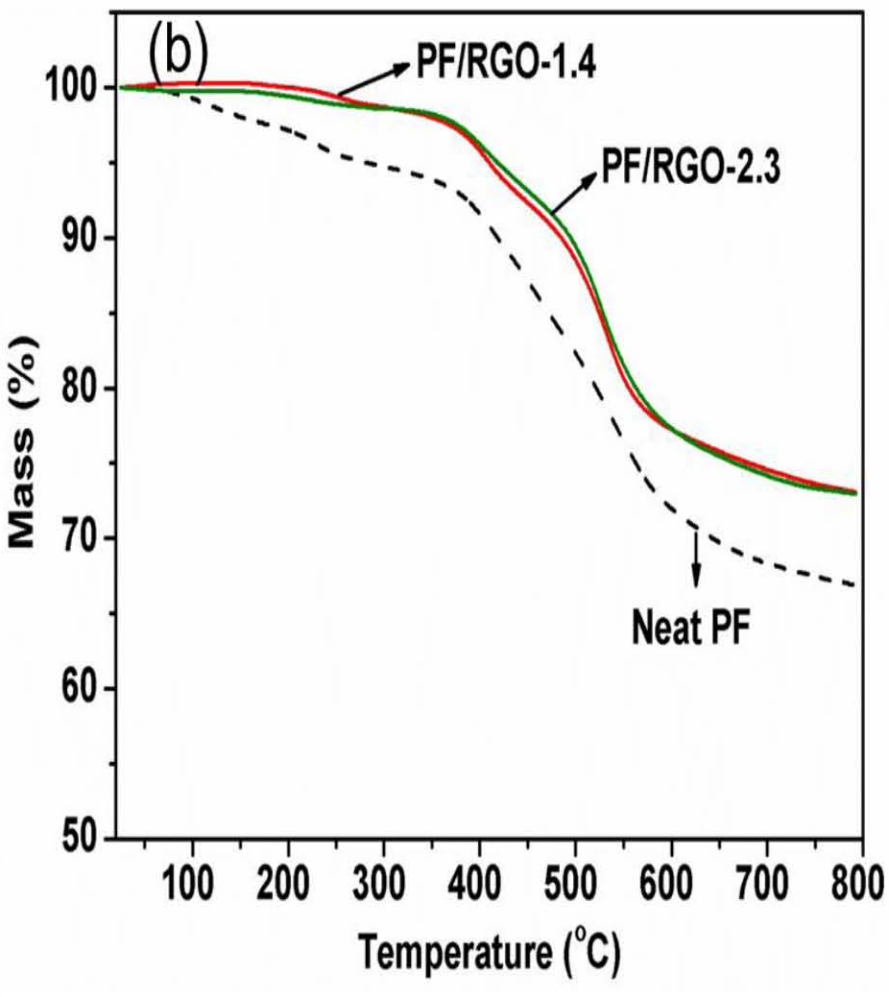
XRD



Reduction and Functionalization of GO

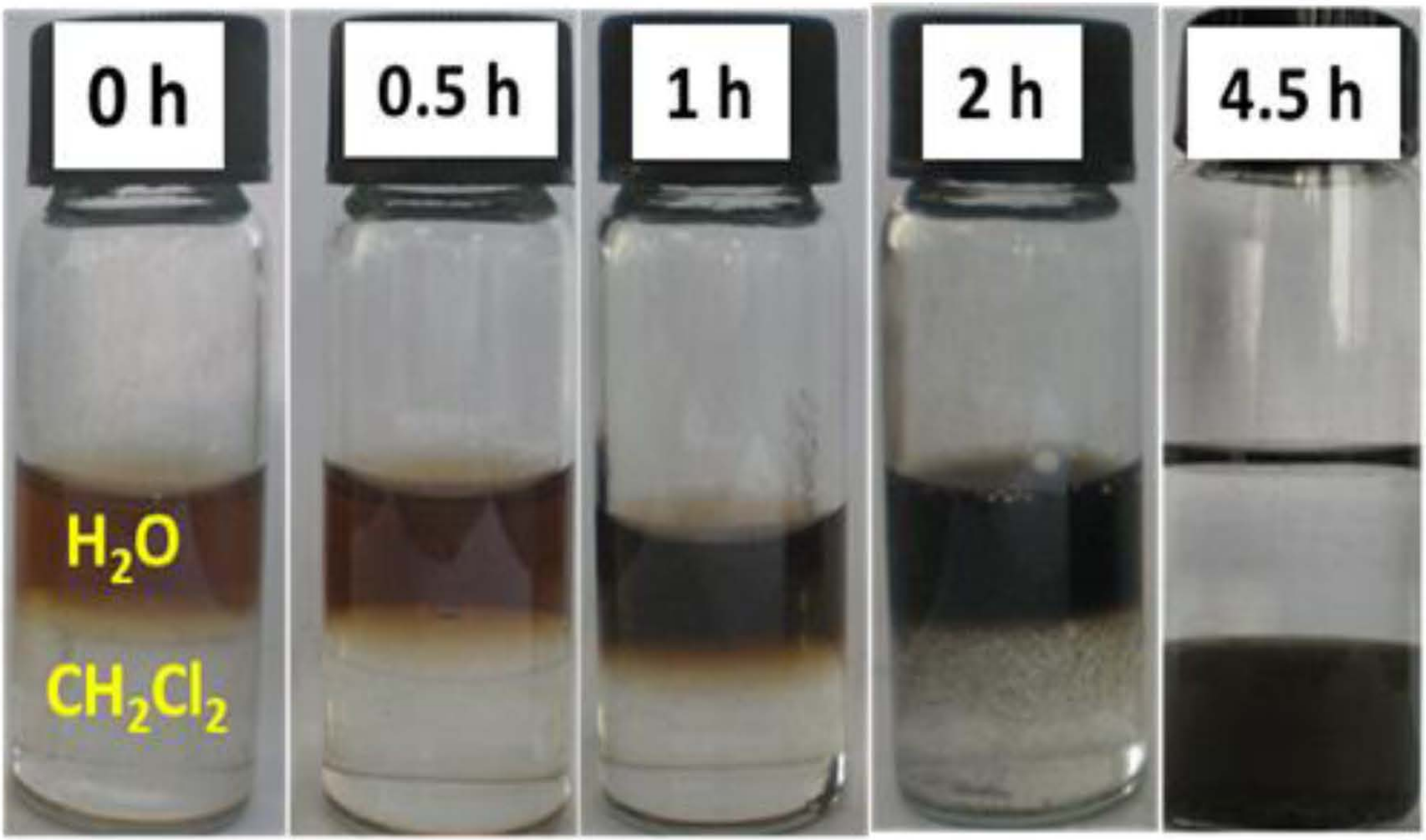
TGA





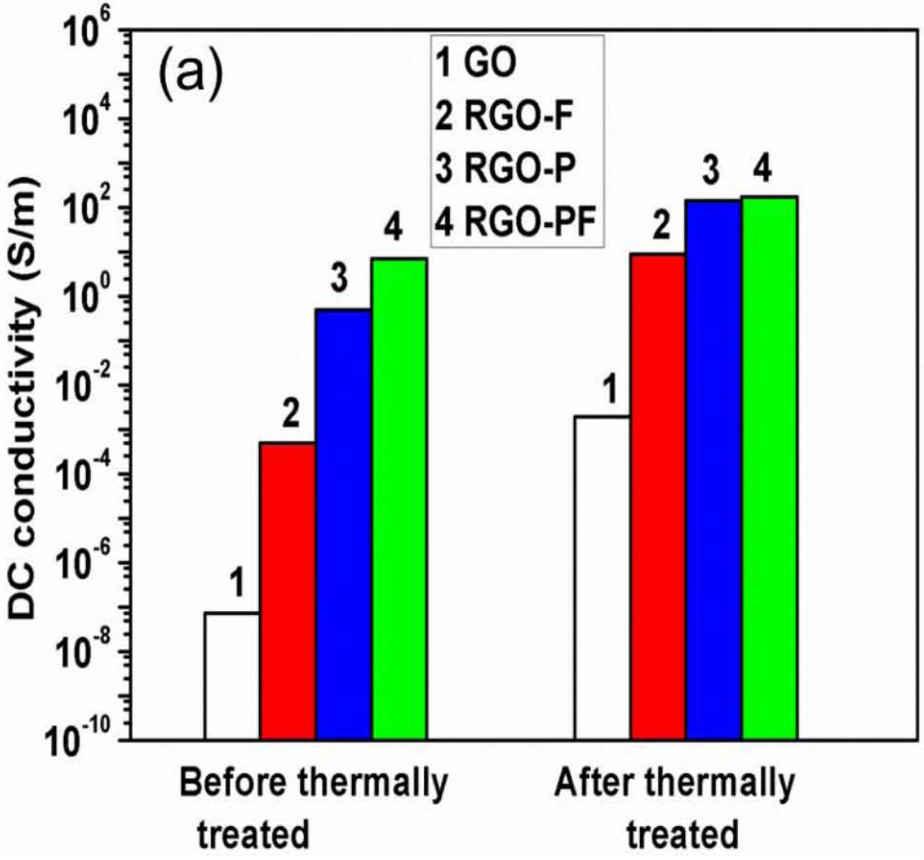
Reduction and Functionalization of GO

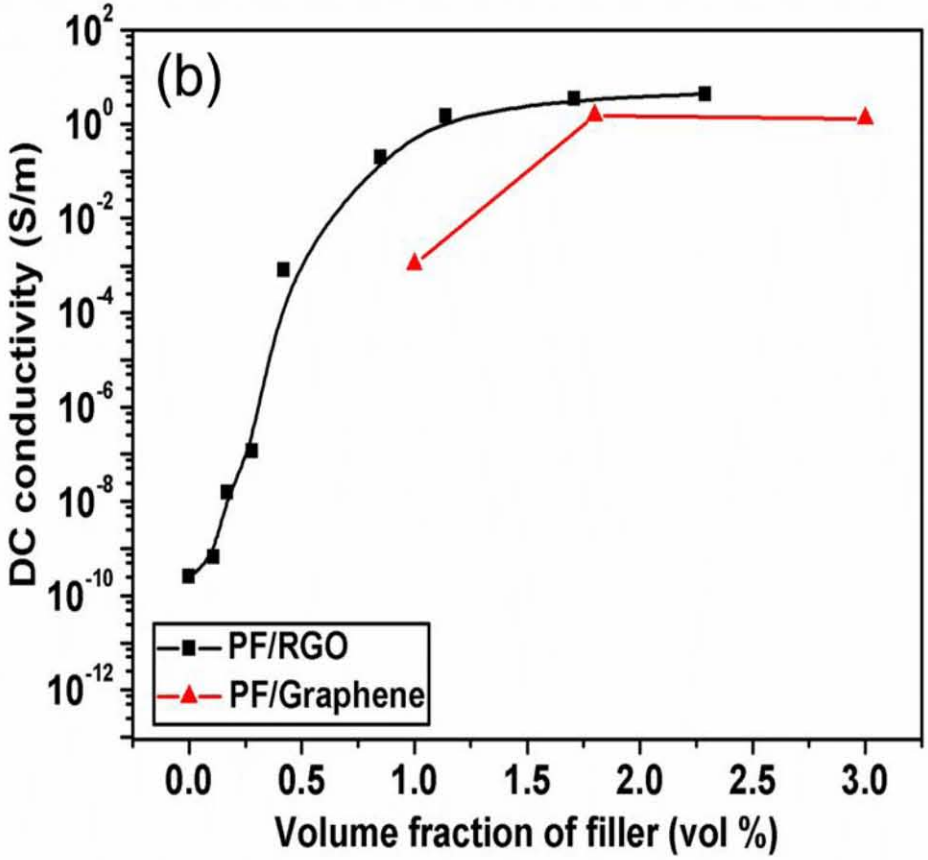
Selective Dispersion of RGO-PF



Improved Electrical Conductivity

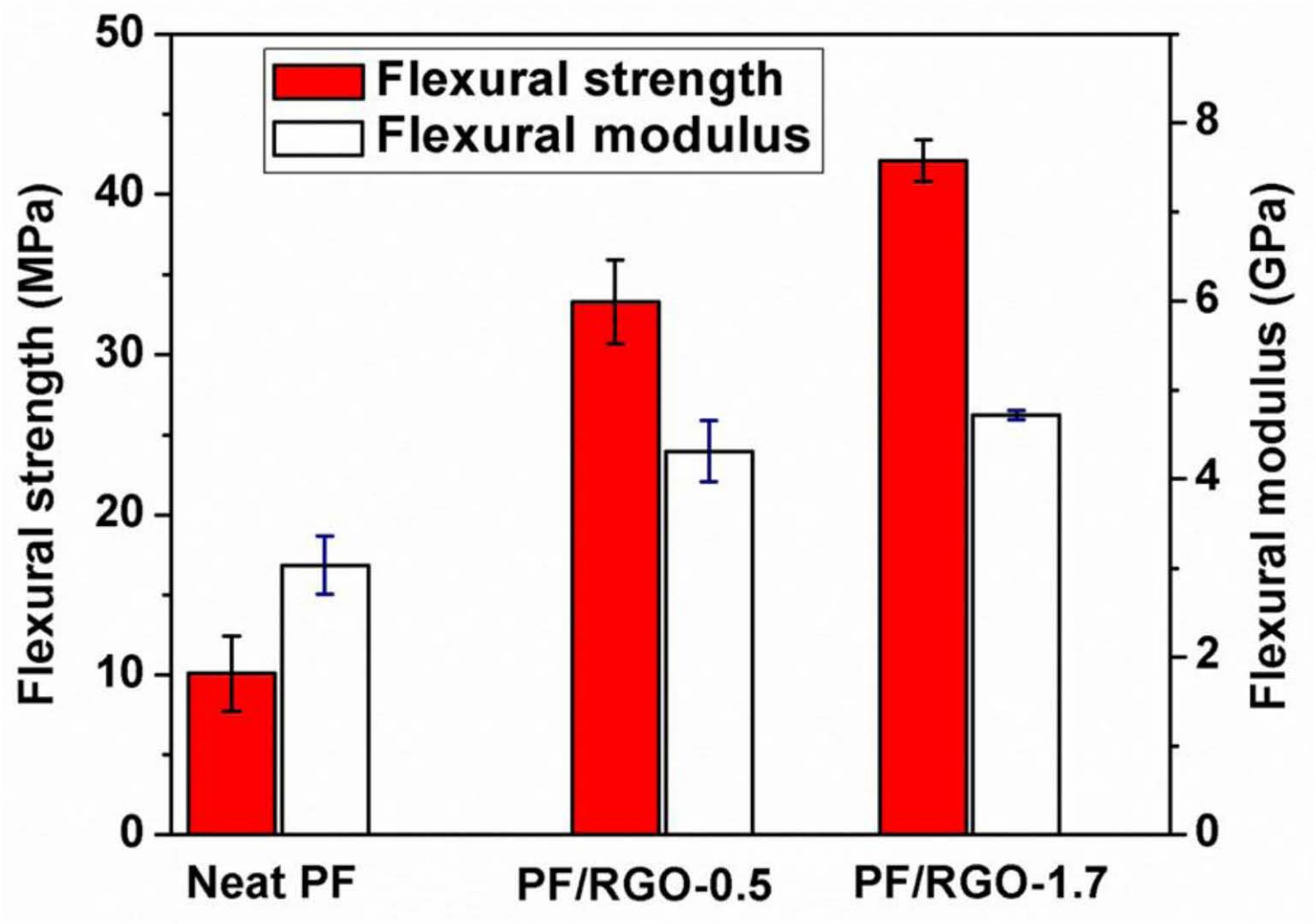
- PF nanocomposites are electrically conductive due to the incidental reduction of GO during in situ polymerization
- No other reducing agent is required



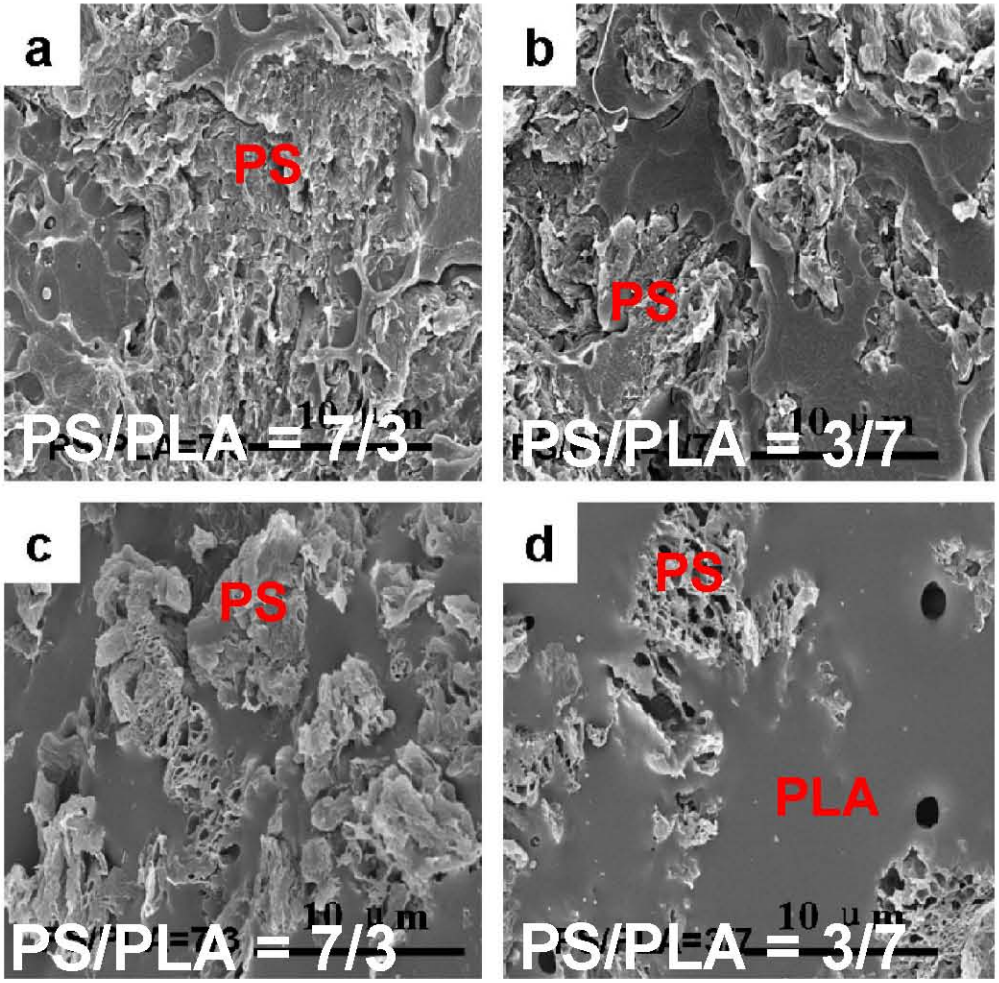


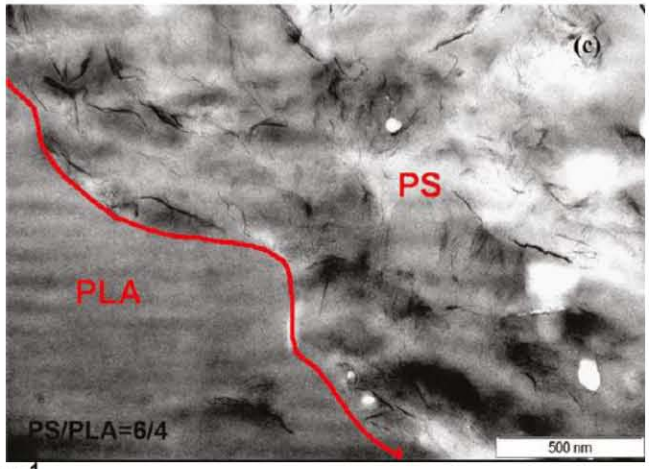
Improved Flexural Properties

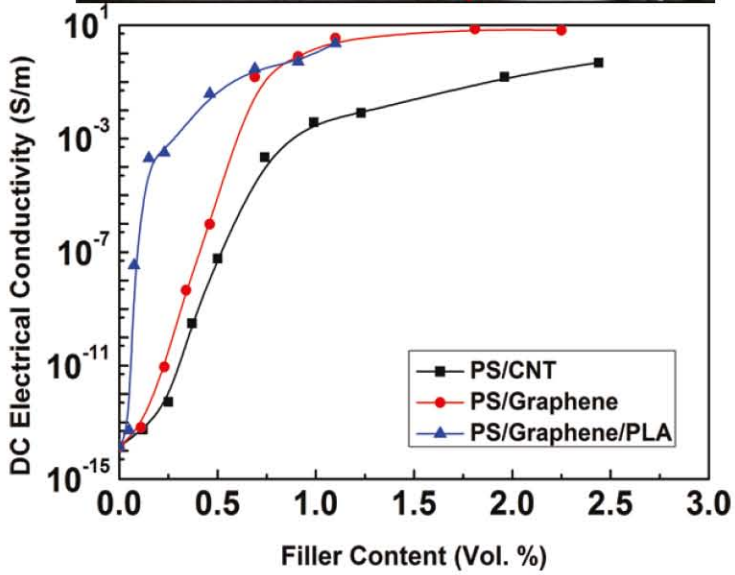
- The presence of RGO improves flexural properties of PF



(5) Higher Electrical Conductivity of PS/PLA Nanocomposites with Less Graphene

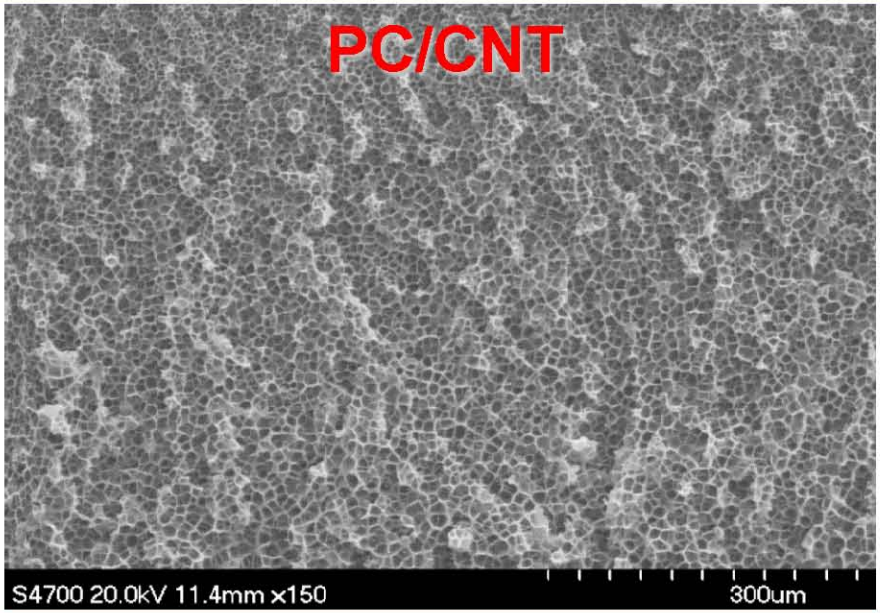


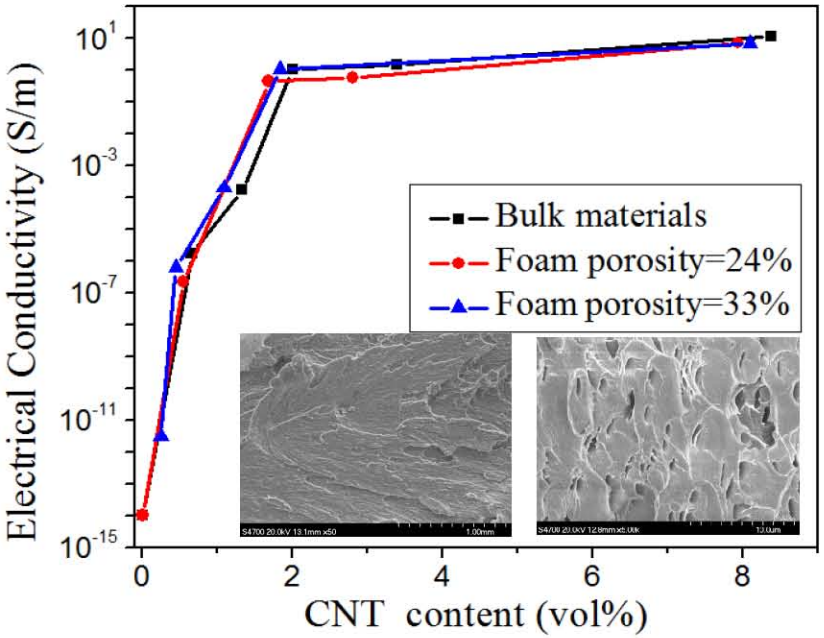


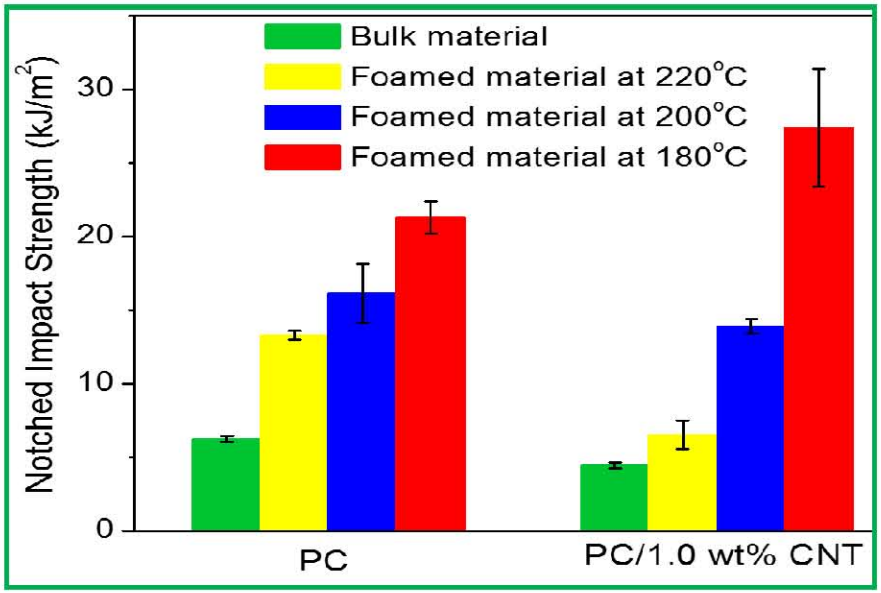


(6) PC/CNT Nanocomposite Foams

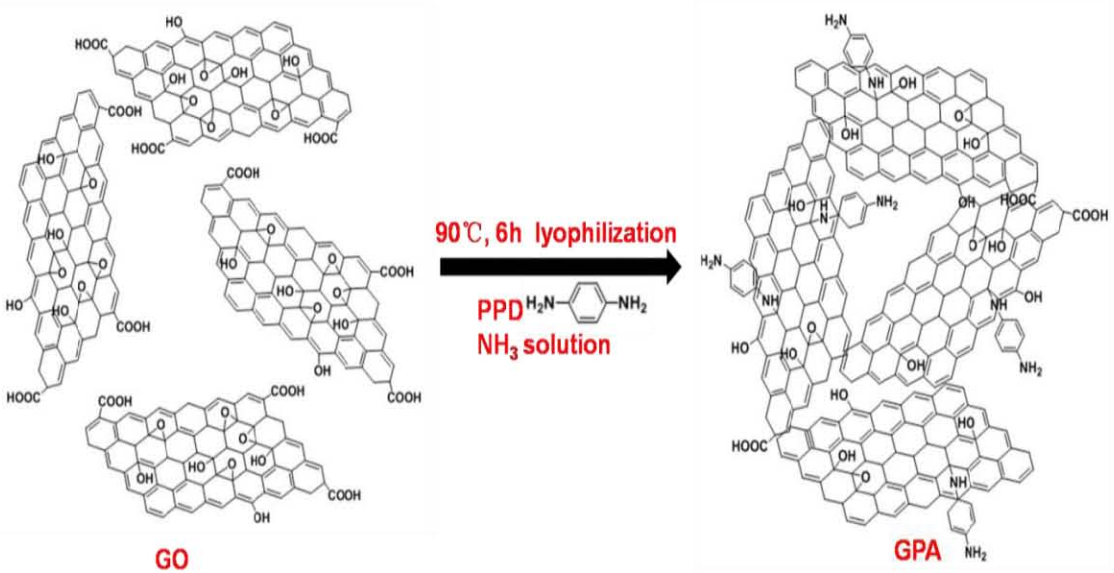
Supercritical CO_2 Foaming

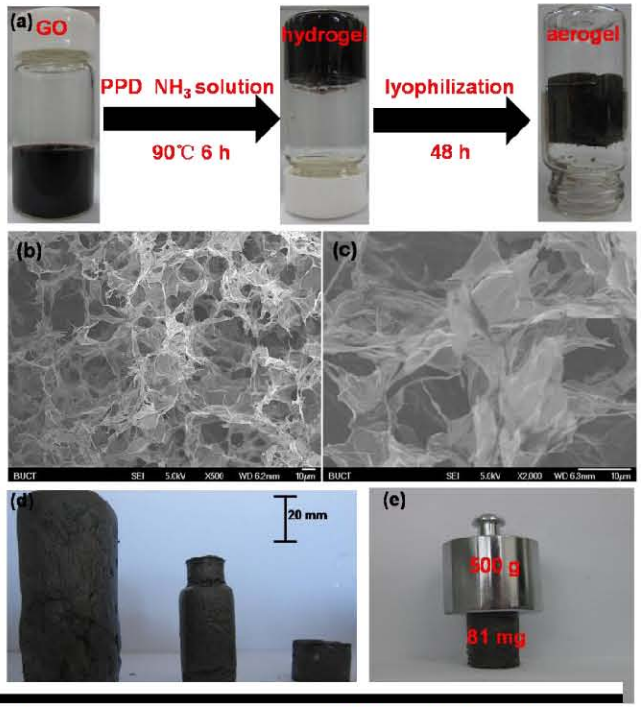






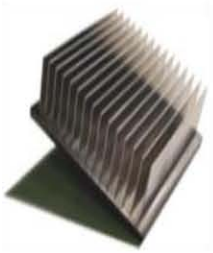
(7) 3D Graphene Aerogels





GO concentration (mg/ml)	Sample	Bulk density (mg/cm^3)	Thermal conductivity (W/mK)	Electrical conductivity (S/m)
1.0	GPA-1	1.8	0.040	1.5×10^{-2}
4.5	GPA-4.5	6.9	0.041	4.3×10^{-1}
10.0	GPA-10	14.2	0.044	5.7×10^{-1}
20.0	GPA-20	27.2	0.053	1.0

5.
Thermally Conductive Polymer Nanocomposites



Folded Fin Heat Sinks

Tubing Applications

Molded Bobbins

LED

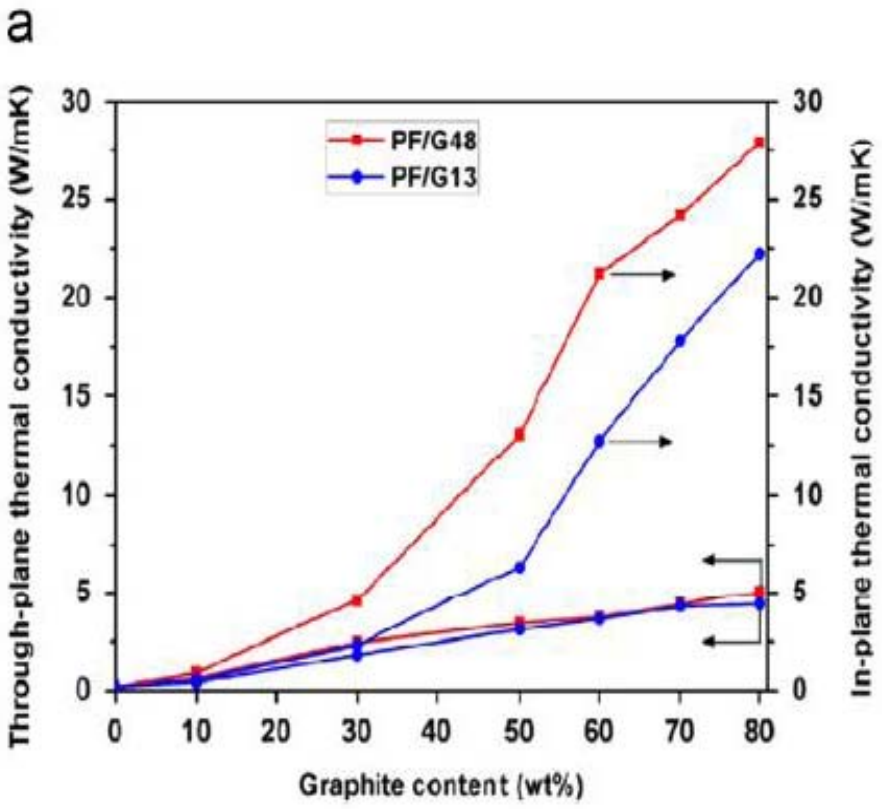
3-D Dielectric Heat Plates for Power Converters

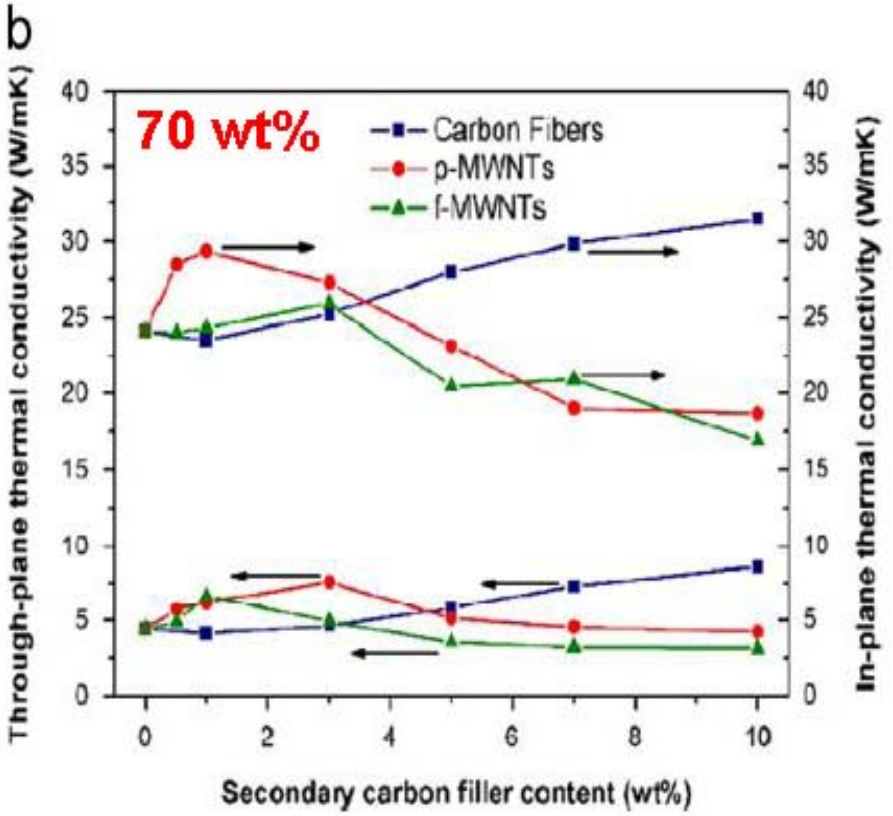
Circuit Boards

Electrostatic dissipation

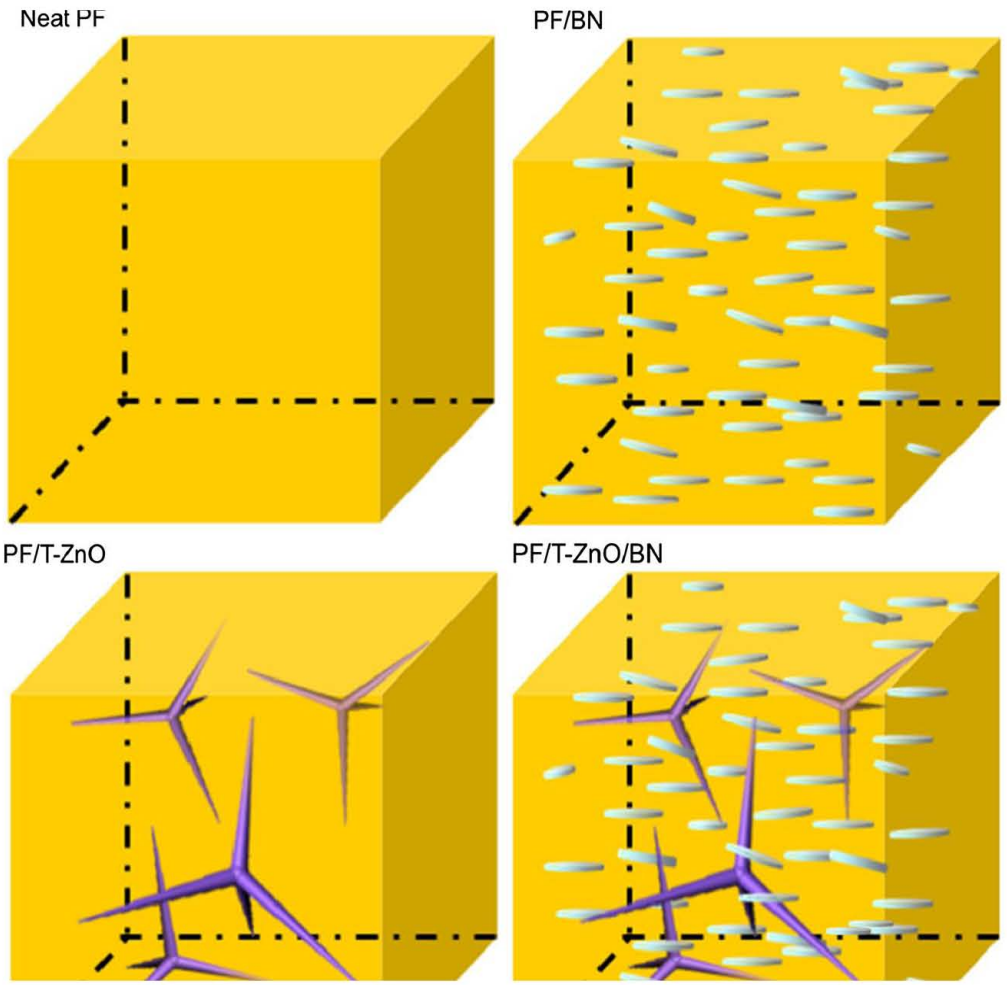
SUBSTRATES ELECTRONIC PACKAGING

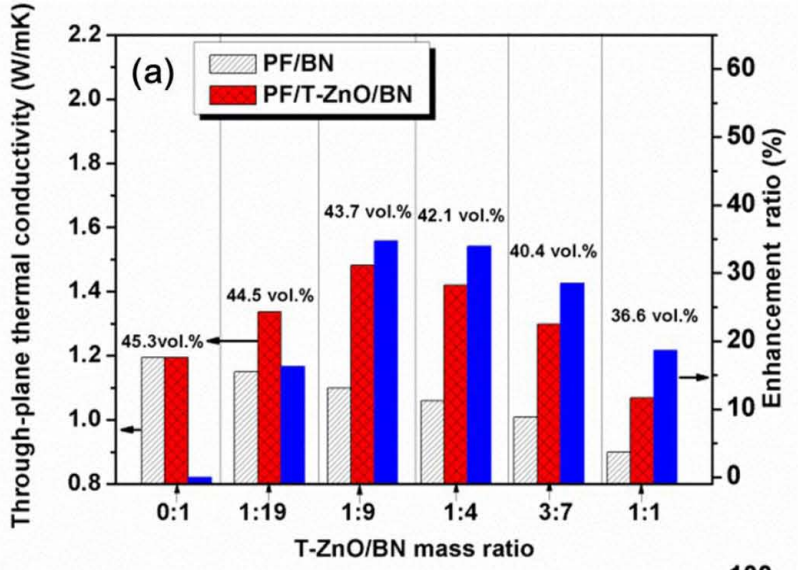
Improved Thermal Conductivity phenol formaldehyde/Graphite Composites

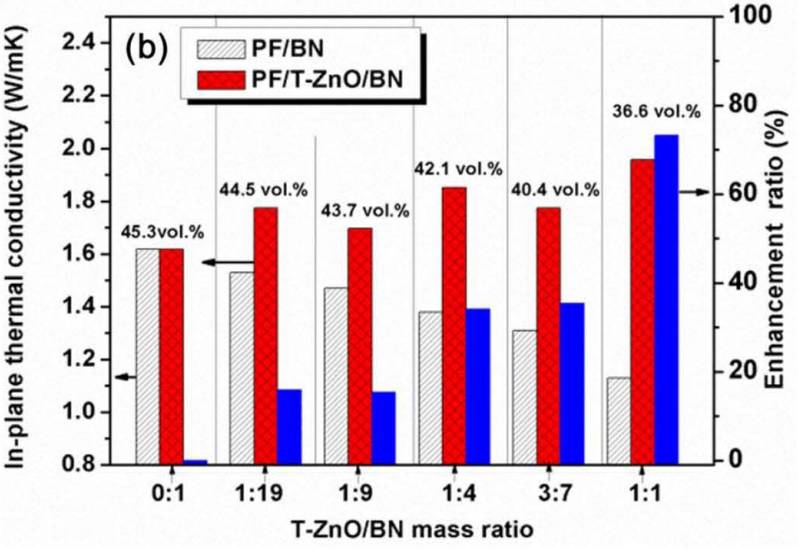




Improved Thermal Conductivity PF/Boron Nitride/Tetrapod Zinc Oxide Composites







Acknowledgements

Prof. Yiu-Wing Mai, University of Sydney, Australia
Prof. Nikhil Koratkar, RPI, USA
Dr. Aravind Dasari, NTU, Singapore
Prof. Wen-Ge Zheng, NIMTE, CAS
Prof. Jin-Yong Dong, ICCAS, CAS
Prof. Maolin Zhai, Peking University
A/Prof. Hao-Bin Zhang, BUCT
A/Prof. Jin Qu, BUCT
Dr. Xiaofeng Li, BUCT
My graduate students

NSFC, MOE, BSTC , BUCT, SKLOIC