Multifunctional Polypropylene Nanocomposites

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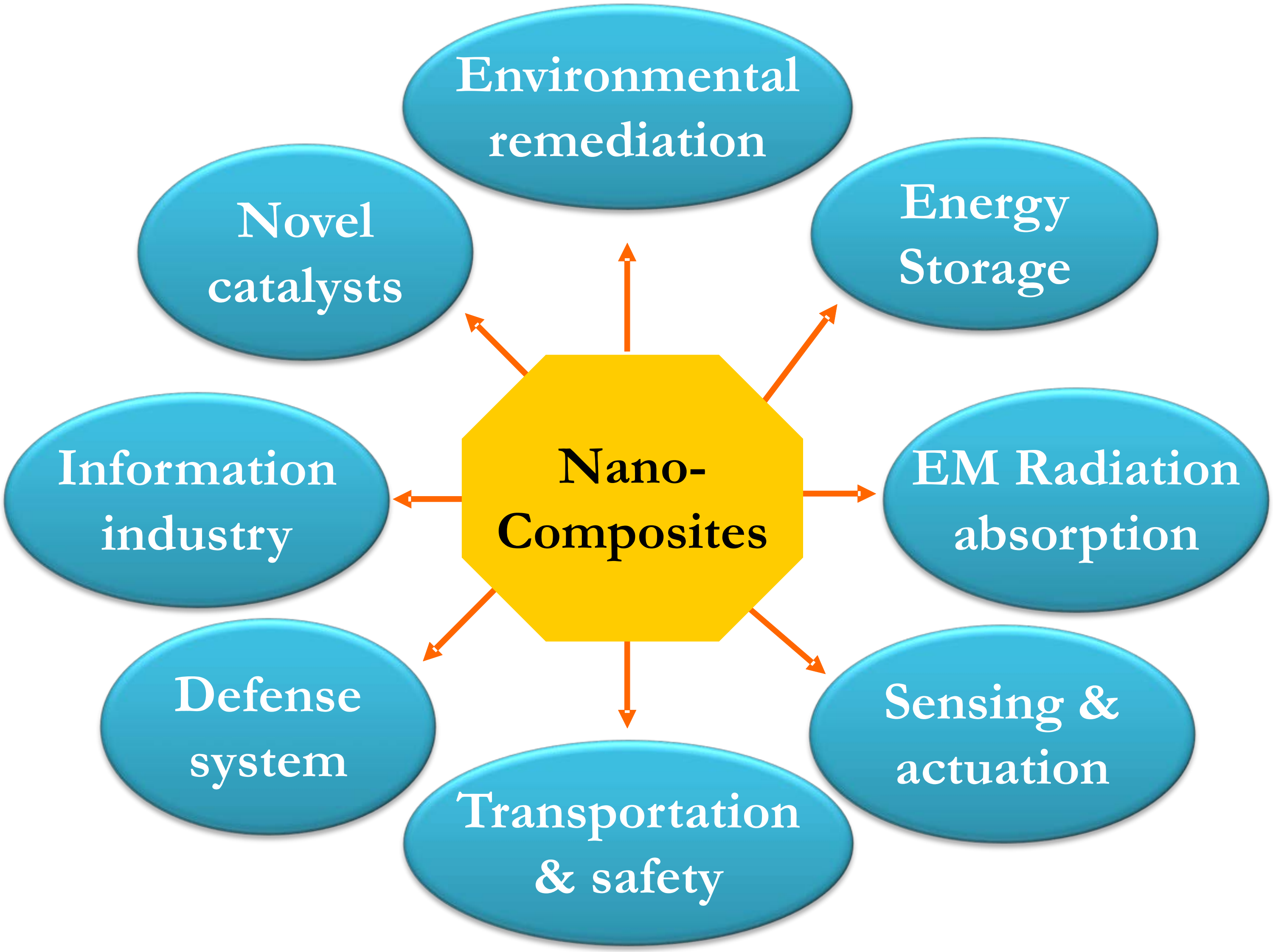

C. Yang, Z. Guo*, *et al.*, *J. Mater. Chem. A.*, 3, 14929-14941 (2015)

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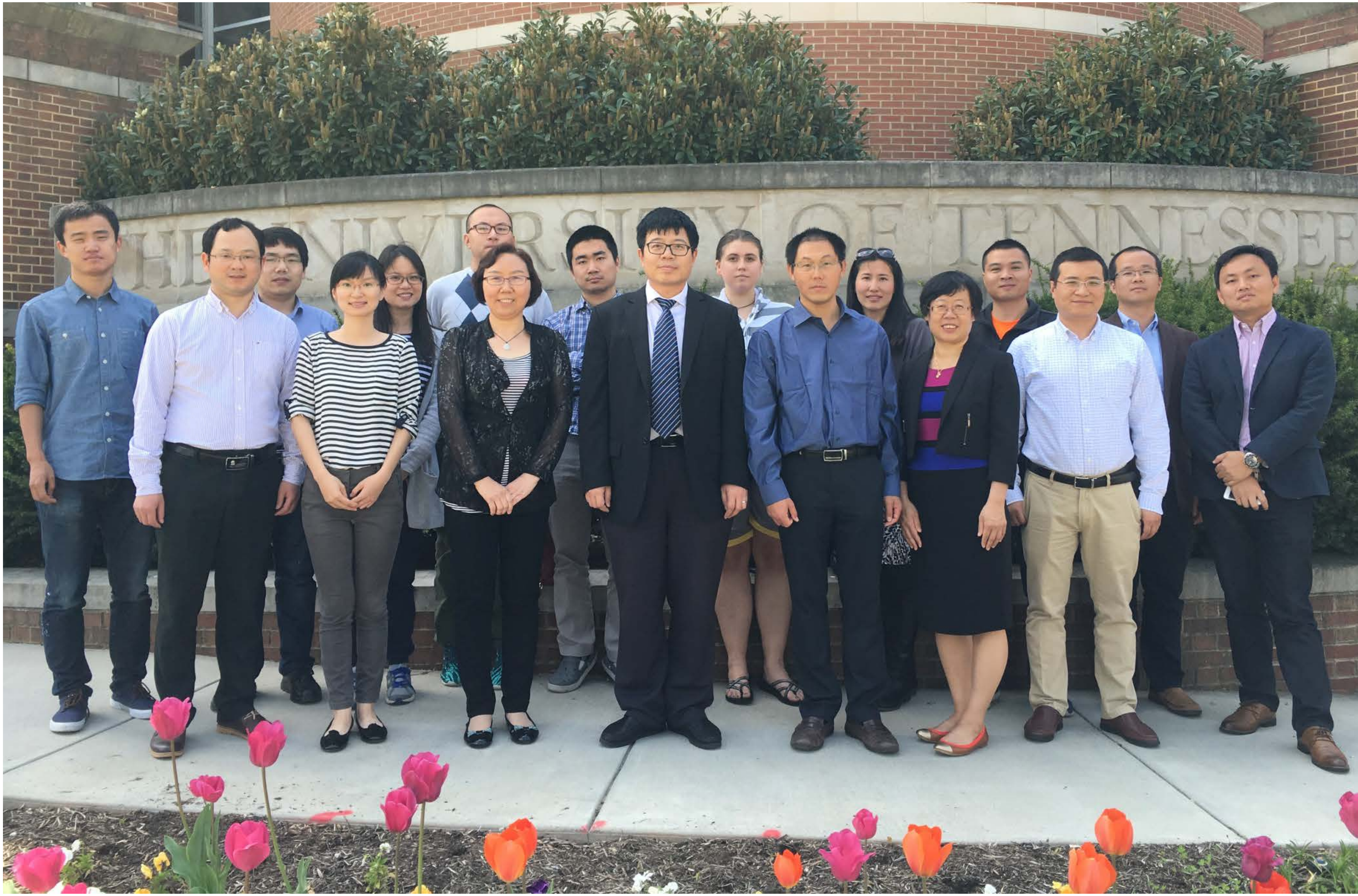

Outline

- Introduction
- Research Work

  Part I: Solvent Surface Coating Method

  Part II: Microwave Radiation Surface Coating Method
- Conclusions
- Acknowledgement

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- **Introduction**
- **Research Work**

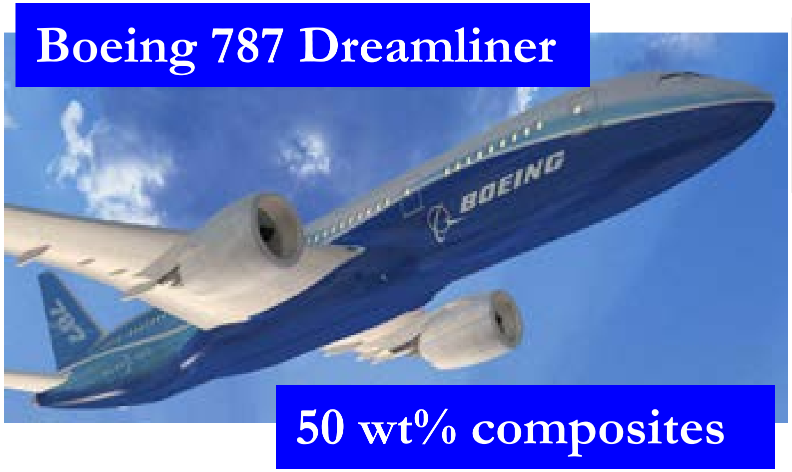
    Part I: Solvent Surface Coating Method

    Part II: Microwave Radiation Surface Coating Method

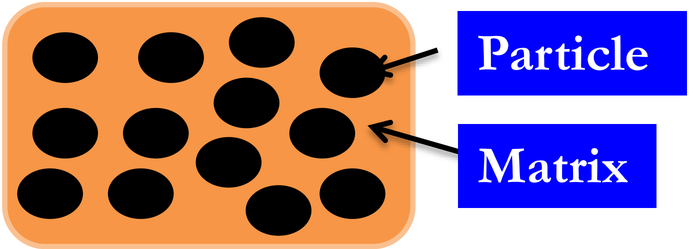
- **Conclusions**
- **Acknowledgement**

Composites and Polymer Nanocomposites (PNCs)

- **Composites:** Two or more materials with different properties remain separate and distinct on a macroscopic level within one unity.



- **Nanocomposites:** *Composites with any dimension in any phase less than 100 nm.*

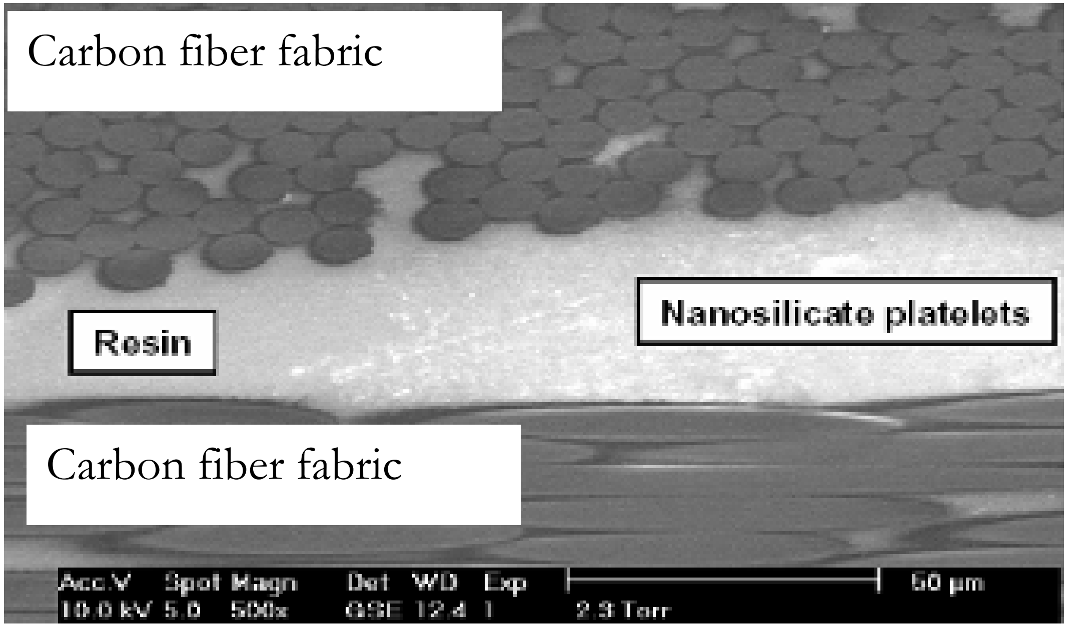


- **Polymer Nanocomposites**

✓ *Lightweight (compared to **metal**)*

✓ *High mechanical properties (compared to **pure resin**)*

✓ *Unique physical and chemical properties*



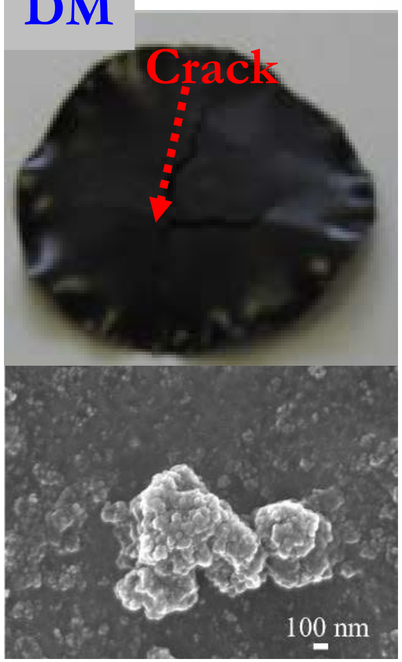
Nanocomposite Fabrication: Challenges

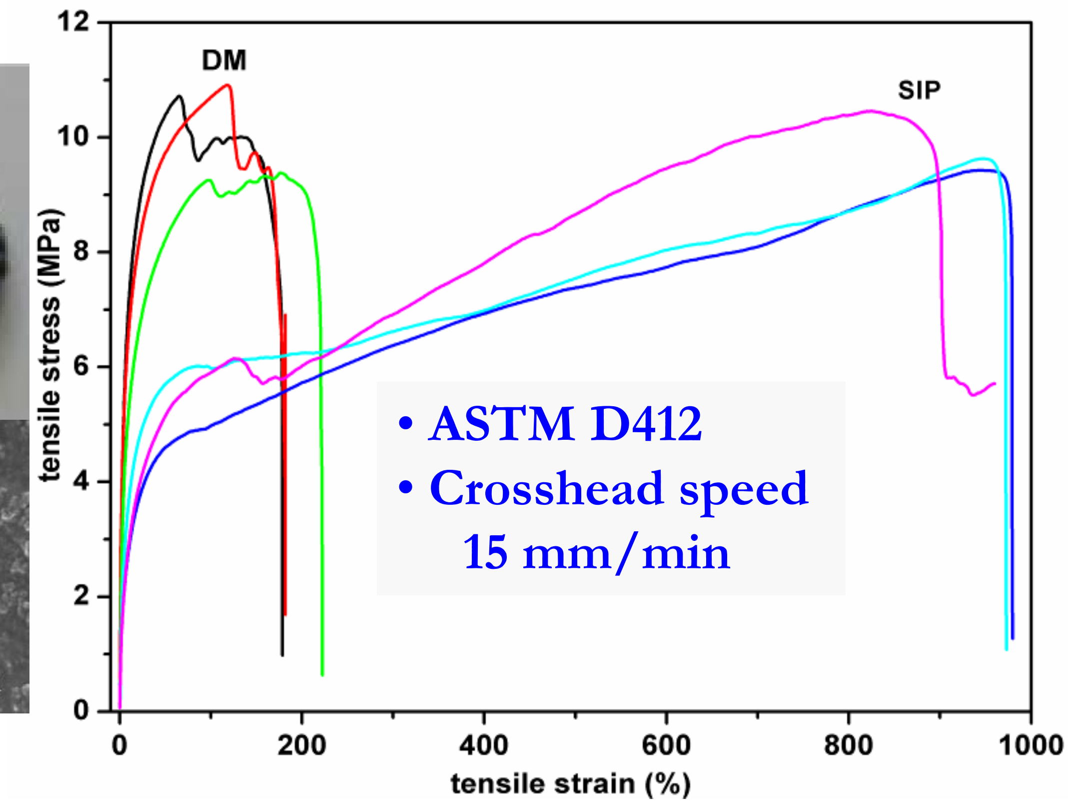
- *Particle/polymer interaction*
- *Particle agglomeration*

Direct-Mixing (DM) **Surface-Initiated-Polymerization (SIP)**

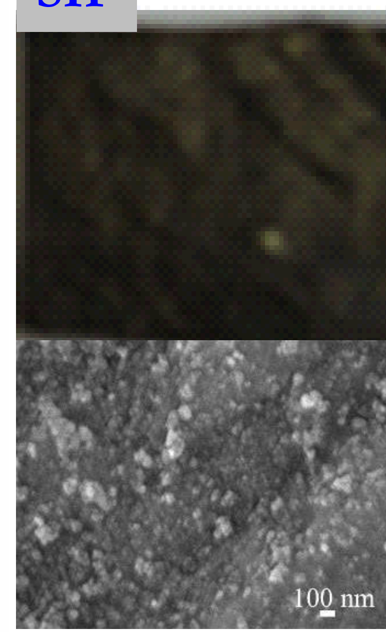
65 wt% Magnetic Polyurethane Nanocomposites

DM





SIP



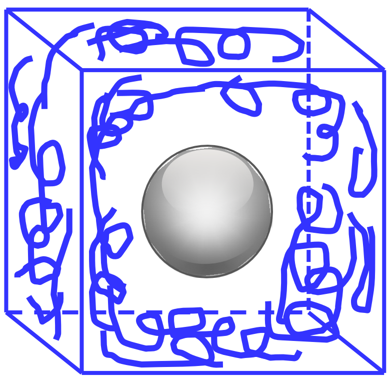
Z. Guo et al., *Nanotechnology*, 18, 335704 (2007)

Motivation

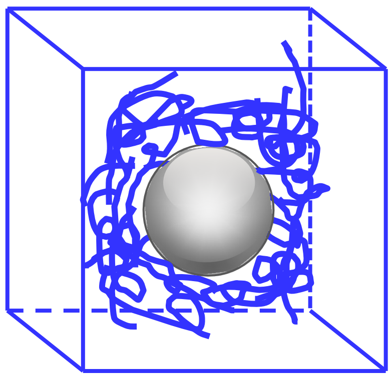
Nanoparticles (NPs)/Polymer Interactions

- *Weak physical adsorption*

Voids

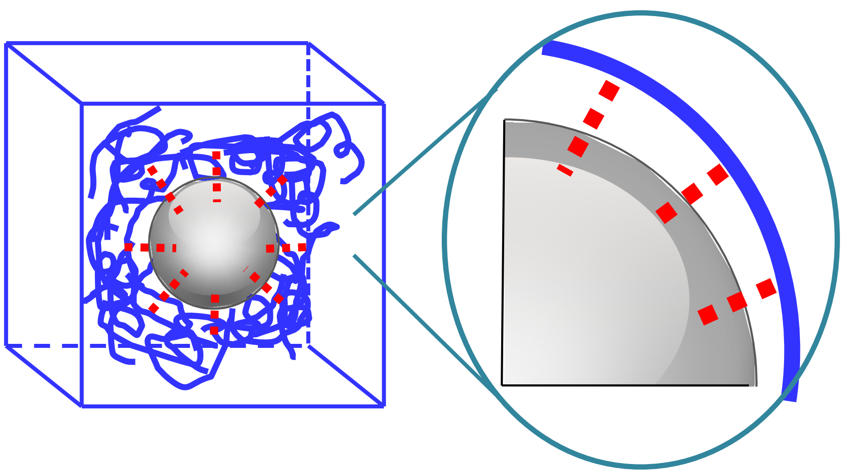


Wrapping



- Minimize the voids
- Enhance the polymer wrapping

- *Strong covalent bonding*



- Increase the bonding density

Control the NPs/Polymer interface nanostructures

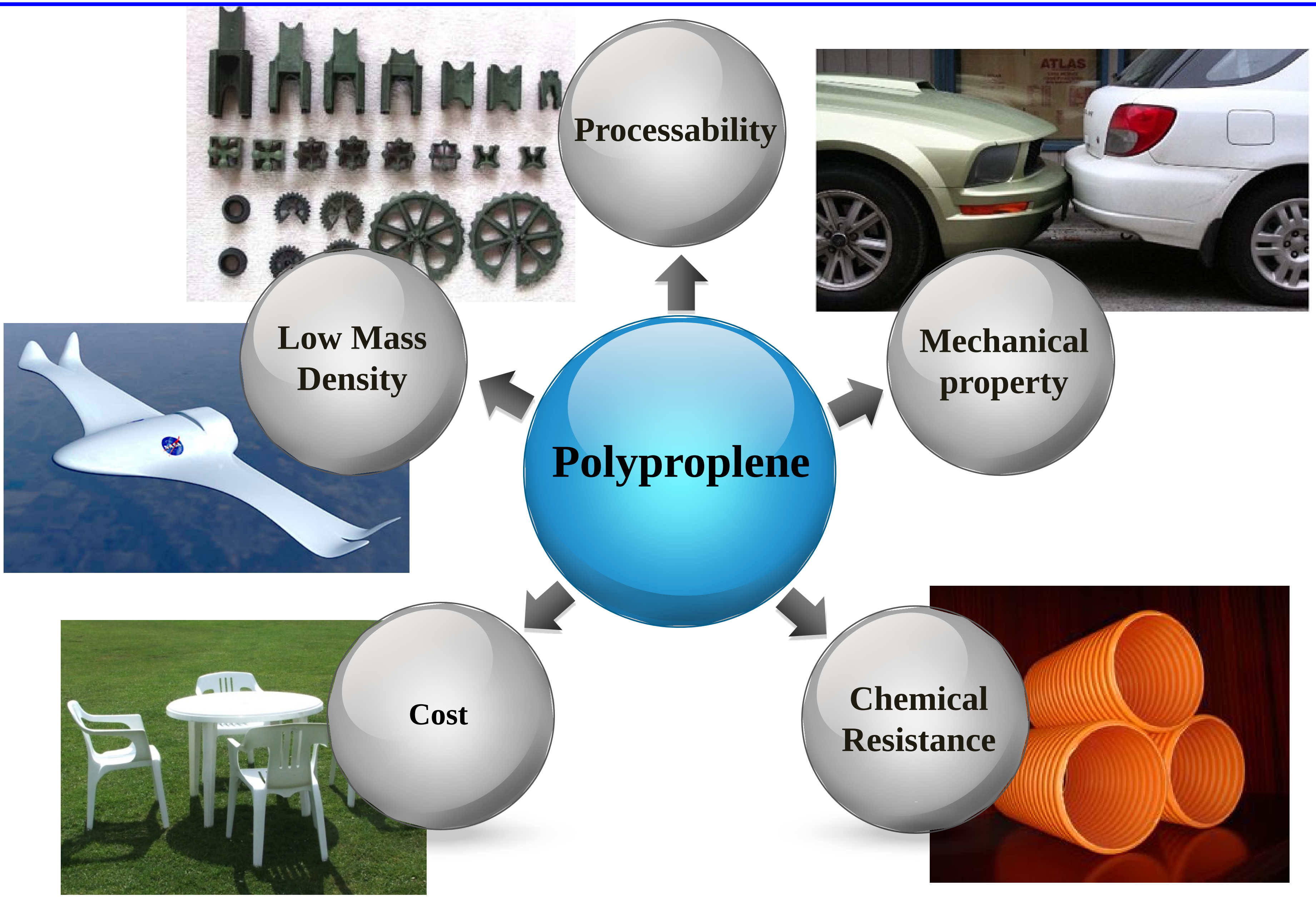
↓

Enhance the Interaction

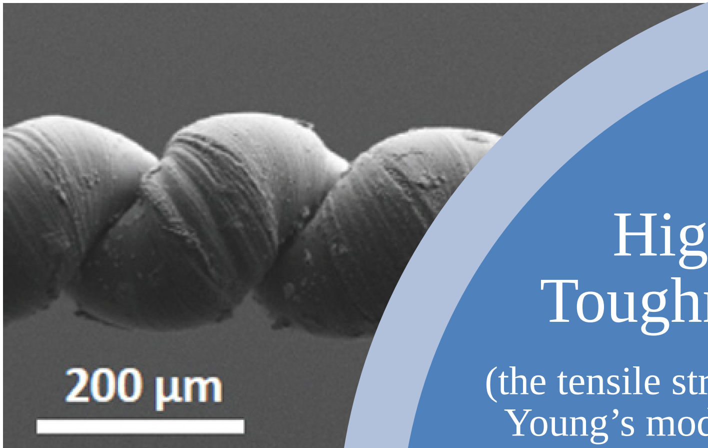
↓

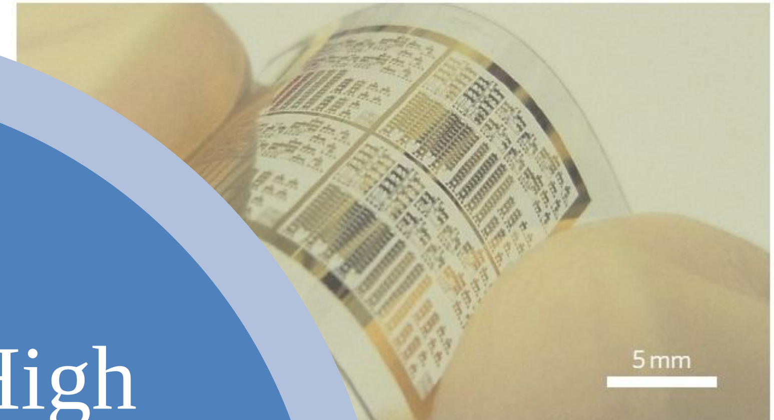
Good Performance

Why Polyproplene (PP)?



Why Carbon Nanotubes (CNTs)?





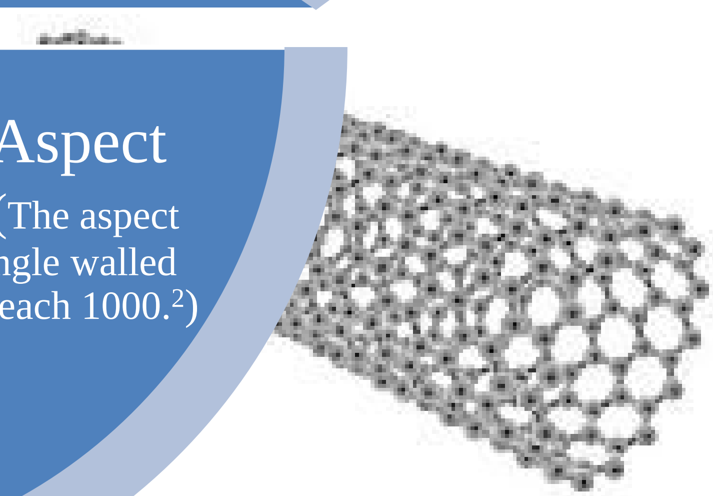
High Toughness

(the tensile strength and Young's modulus can reach to 63 GPa and 950 GPa, respectively.[1])

High Flexibility

Low Mass Density

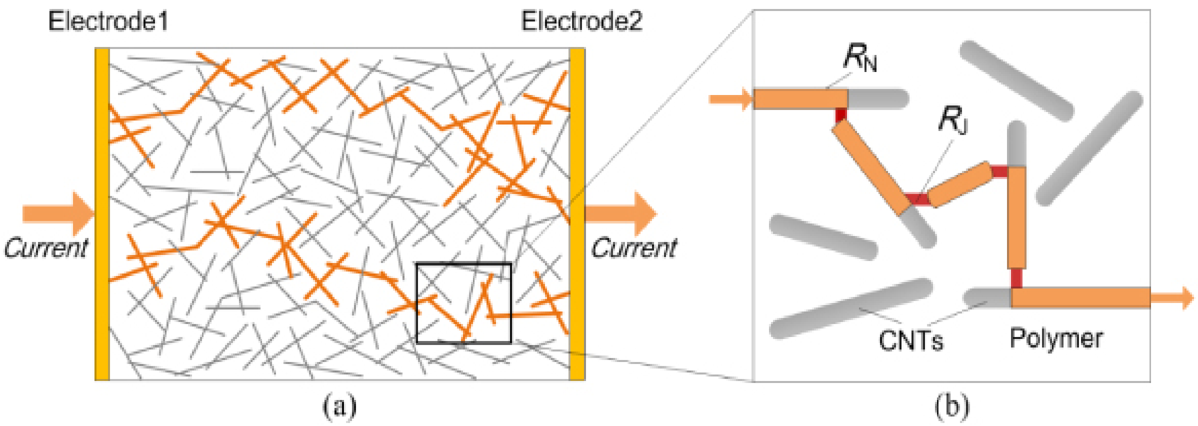
High Aspect Ratio (The aspect ratio of single walled CNTs can reach 1000.[2])

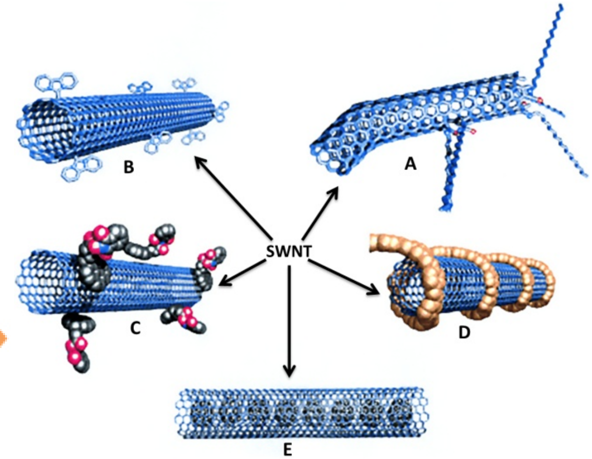


1. Yu; Lourie; Dyer; Moloni; Kelly; Ruoff, *Science, 287, 637-640 (2000)*
2. Biercuk; Llaguno; Radosavljevic; Hyun; Johnson; Fischer, *Appl. Phys. Lett., 80, 2767-2769 (2002)*

Challenges

➢**High CNTs content was required** to accomplish the conductive network in polymer



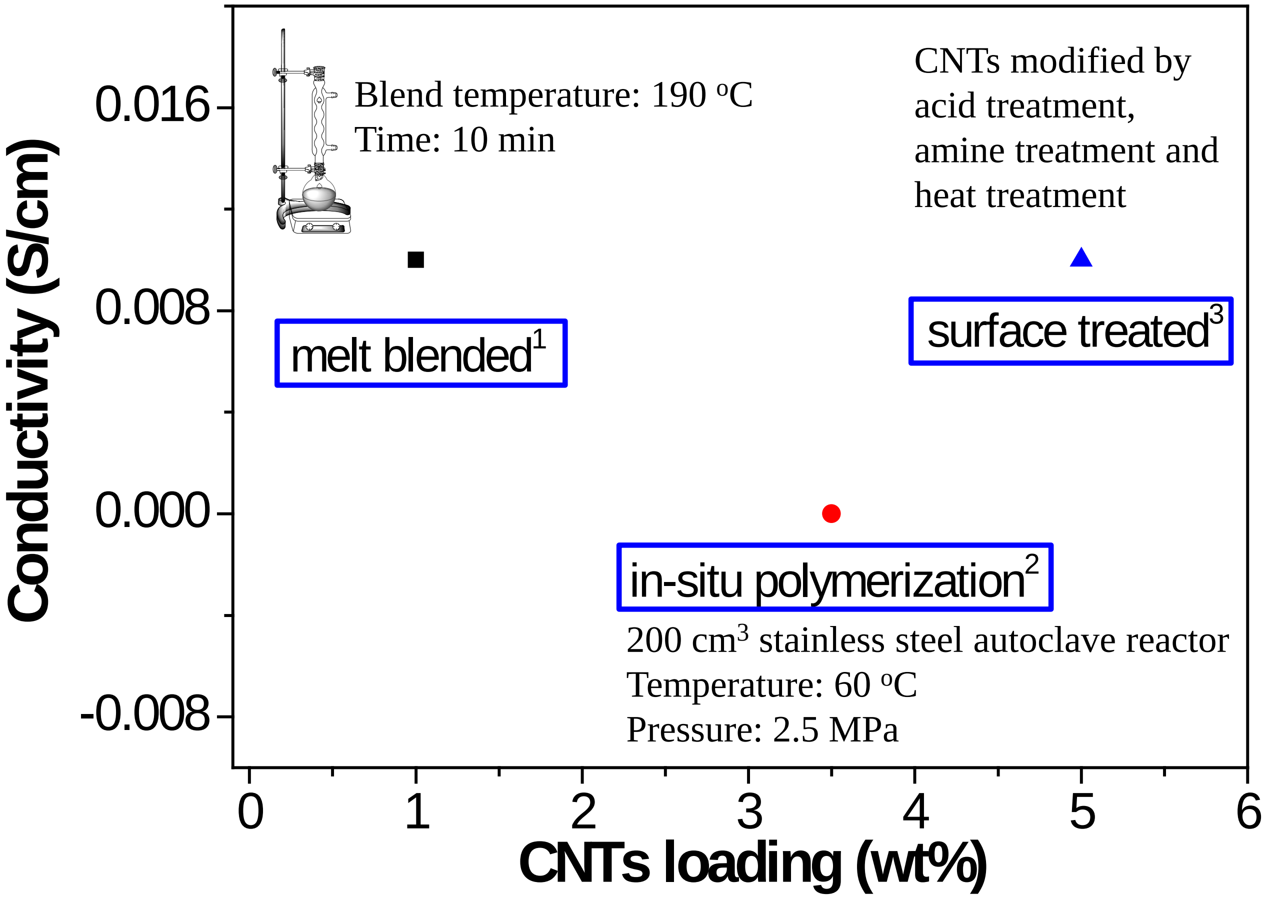


➢Chemically functionalized through acid, amine and heat treatment.[1]

➢Negative effect on the conductivity of the pristine CNTs by influencing the connection.[2]

1. Lee; Cho; Jeon; Youn, *Carbon, 45, 2810-2822 (2007)*
2. Bose; Khare; Moldenaers; *Polymer, 51, 975-993 (2010)*

Current Situation



➢**Limited** electrical conductivity can be obtained

Is there any other efficient way to achieve the conductive network of the CNTs in the polymer matrix?

1. Seo; Park, *Chem. Phys. Lett., 395, 44-48 (2004)*
2. Koval'chuk ; Shchegolikhin; Shevchenko *at al., Macromolecules, 41, 3149-3156 (2008)*
3. Lee; Cho; Jeon; Youn, *Carbon, 45, 2810-2822 (2007)*

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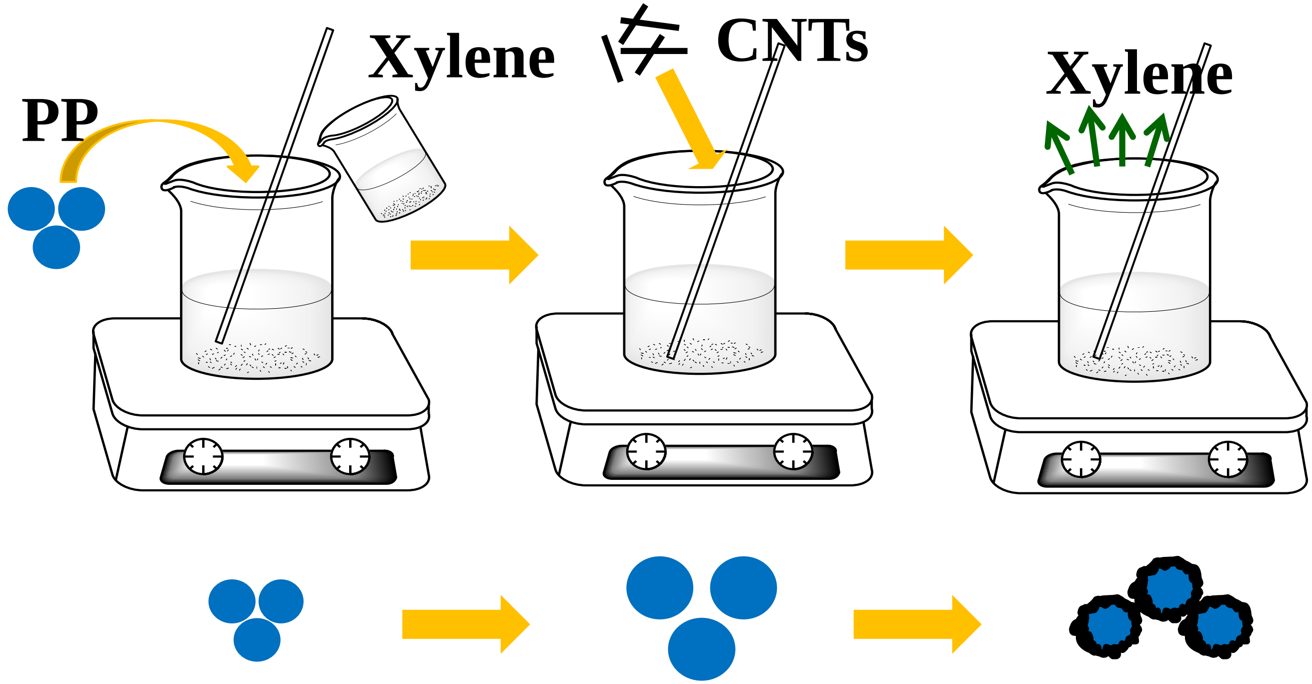
Fabrication Procedure



PP particles are dispersed in xylene at 70 °C

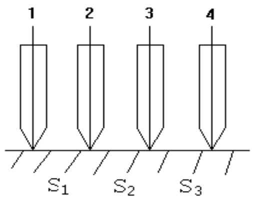
After the PP particles are swelling in the xylene CNTs are added to the solution

Let xylene vaporize after the PP particles are wrapped with CNTs

The PP/CNTs pellet were hot pressed at 120, 160 and 180 ° C

Electrical Conductivity (σ)

- **Four – probe Technique**



$$\rho = \frac{V \times 2\pi}{I \times \left(\frac{1}{S_1} + \frac{1}{S_2} - \frac{1}{S_1 + S_2} - \frac{1}{S_2 + S_3}\right) \times CF}$$

ρ: Electrical resistivity (Ω cm)
V: Potential difference between inner probes (V)
I: Electrical current (A)
S_n: Distance between the two adjacent probes (cm)
CF: Correction factor

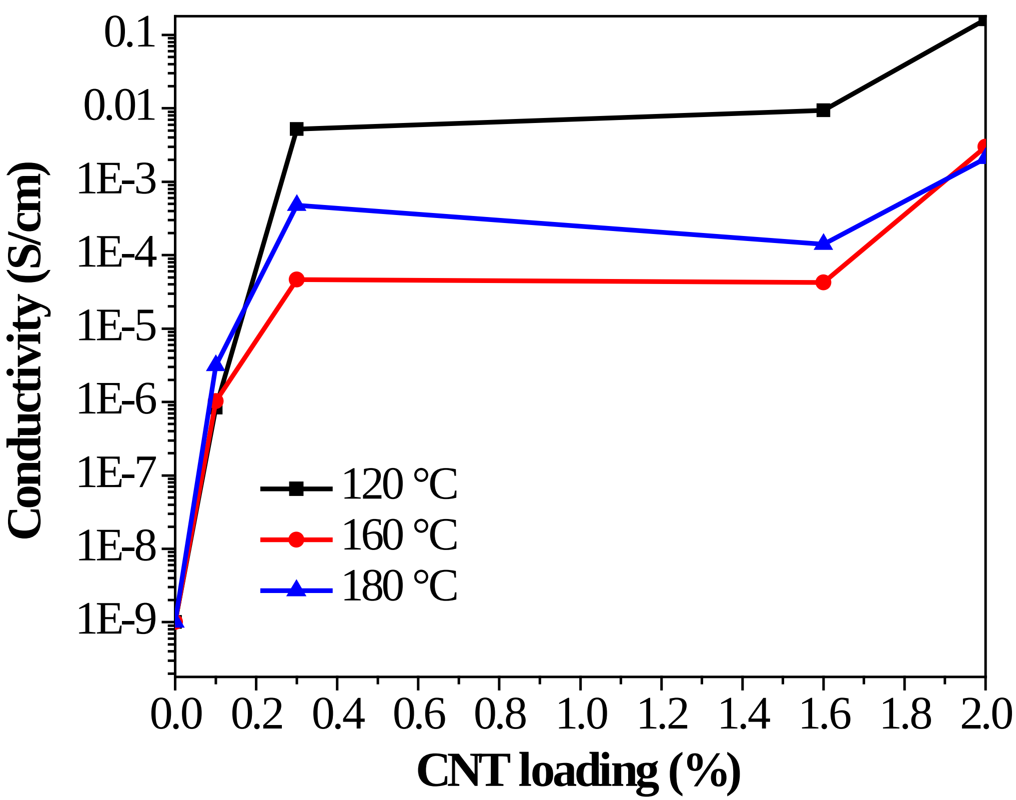
$$CF = 1 + 4\frac{S}{W}\sum_{n=1}^{\infty}\left(\frac{1}{\sqrt{\left(\frac{S}{W}\right)^2 + 4n^2}} - \frac{1}{\sqrt{\left(\frac{2S}{W}\right)^2 + 4n^2}}\right)$$

S: Average distance among the probes
W: Thickness of the sample

$$\sigma = 1/\rho$$

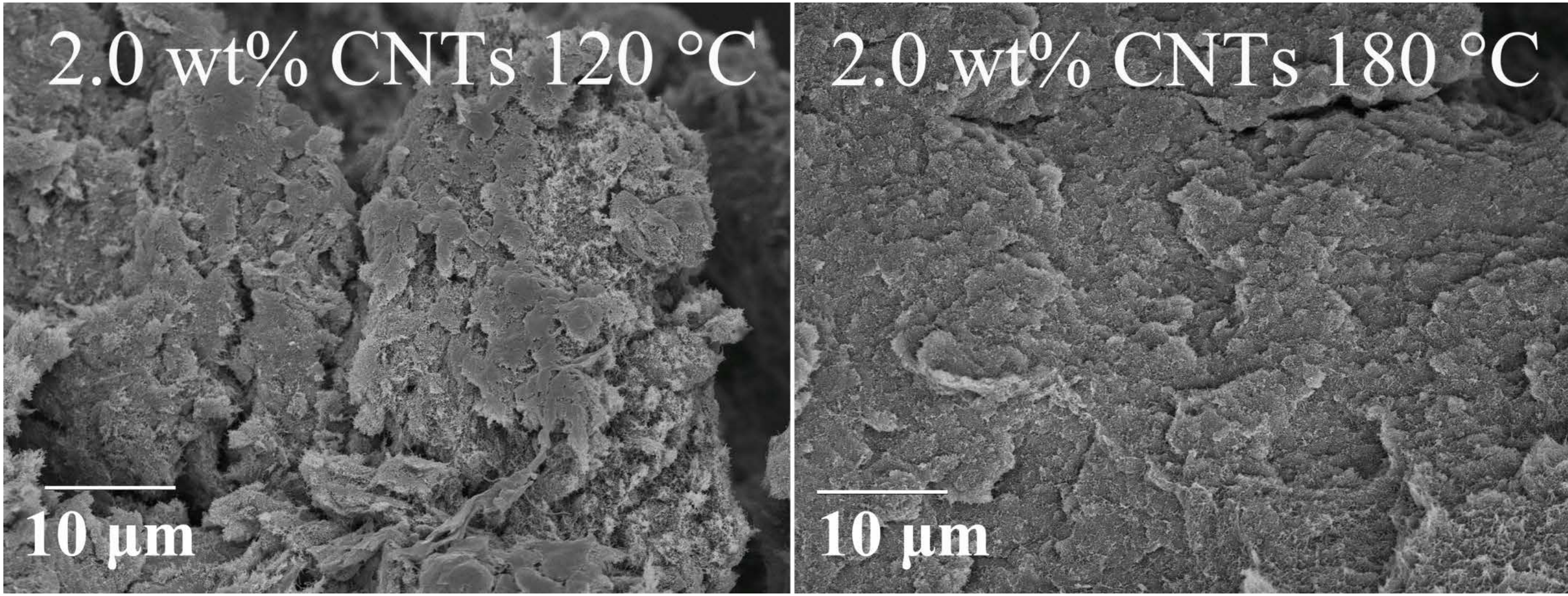
σ: Electrical conductivity (S/cm)

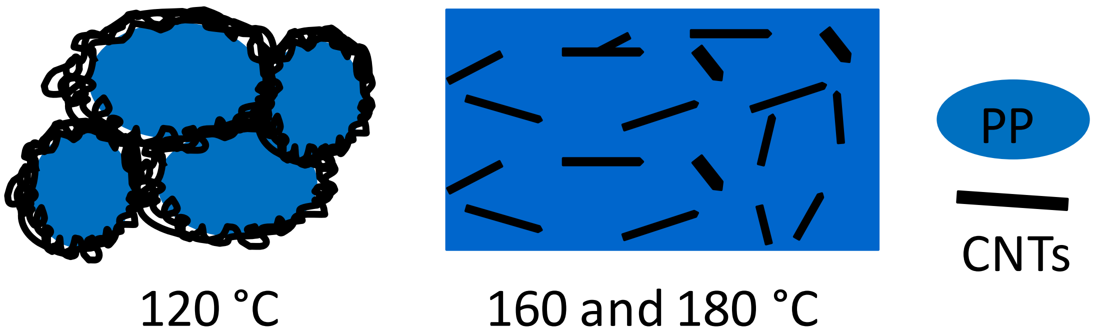
0.16 S/cm



- **Typical percolation behavior can be achieved with only 0.3 wt% CNTs**
- **Ultra higher conductivity value (0.16 S/cm) is observed with low loading of CNTs (2.0 wt%)**

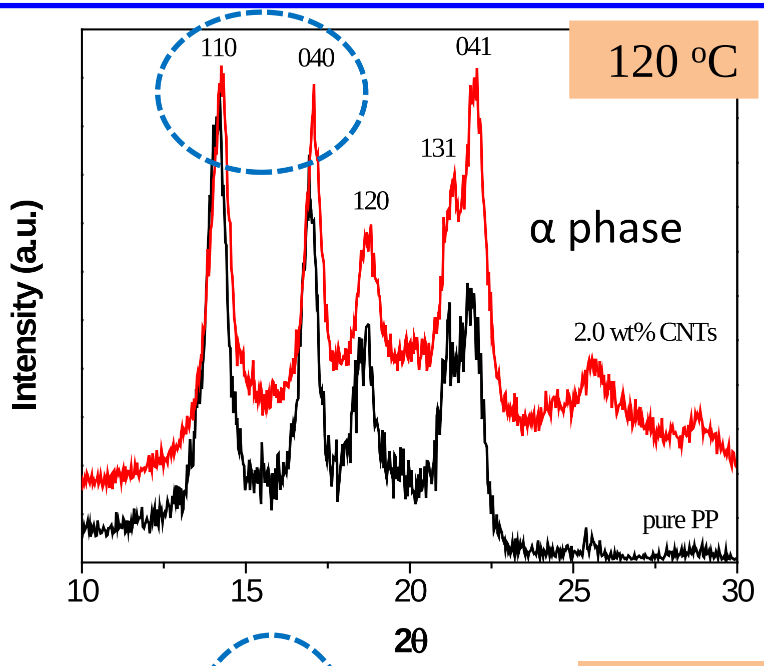
Morphology Study (SEM of fracture surface)

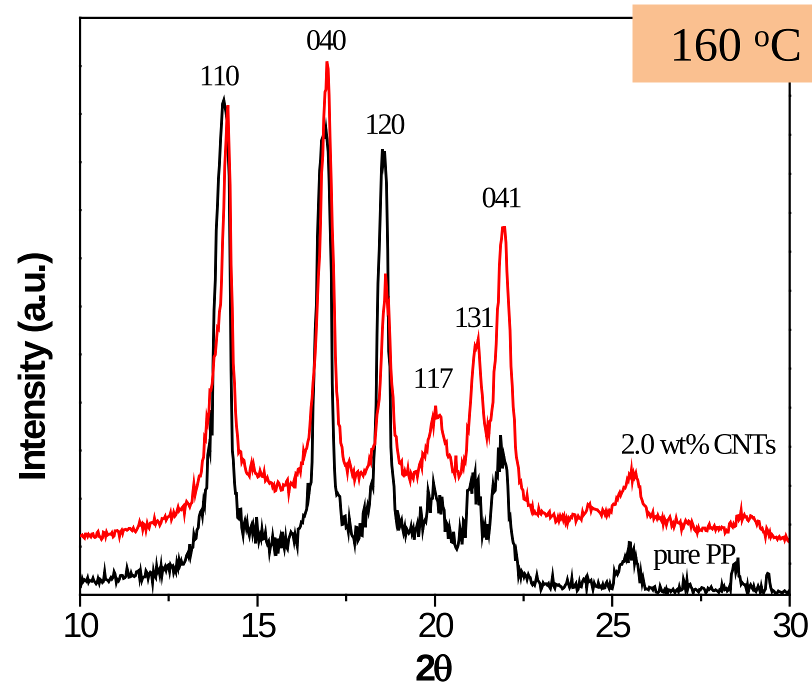


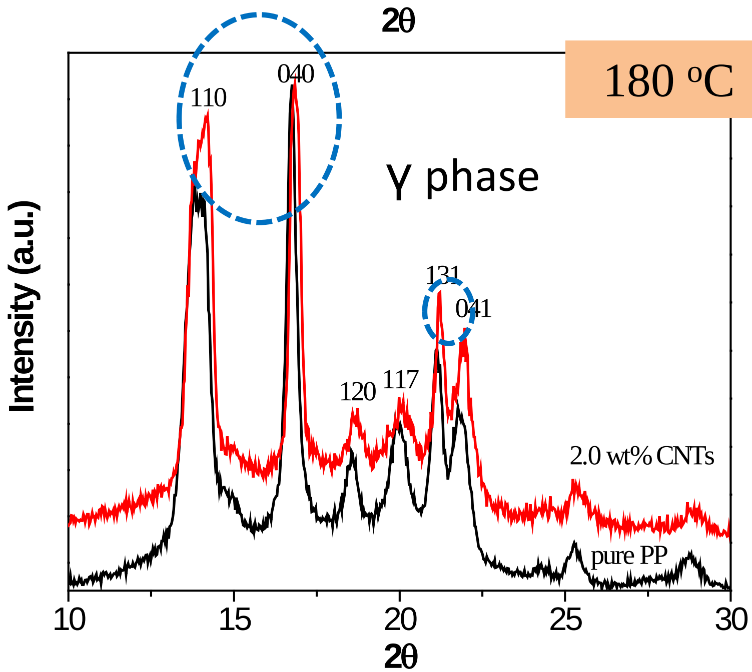


- **The outstanding electric conductivity is attributed to the unique network formation of CNTs in PNCs**

Crystal Structure Study







- **PNCs change from α phase to γ phase with increasing hot pressed temperature**

Crystal Structure Study

The amount of γ phase PP (X_γ) was calculated[1]:

$$X_\gamma = h_\gamma / (h_\gamma + h_\alpha)$$

h_γ and h_α are the peak height at 2θ= 20.07 and 18.5° for the (117) and (131) peak, respectively.

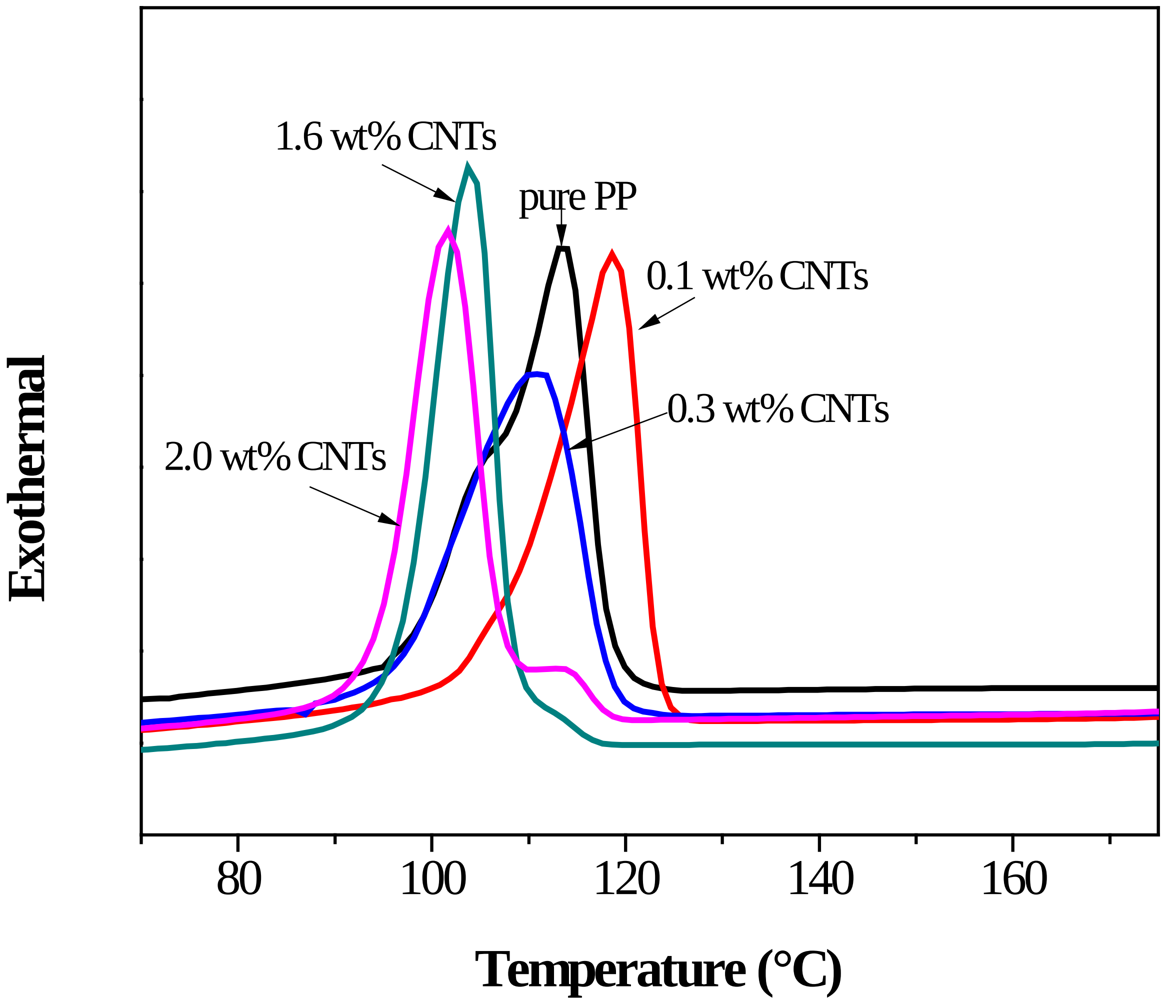
Amount of γ phase PP of pure PP and its PNCs with CNTs.

Samples	120 °C	160 °C	180 °C
Pure PP	N/A	0.1168	0.5770
2.0 wt% CNTs	N/A	**0.2533**	**0.6276**

- **CNTs promoted the γ phase PP formation.**

1. Thomann; Wang; Kressler; MÃlhaupt, Macromolecules, 29, 8425-8434 (1996)

Crystallization Study



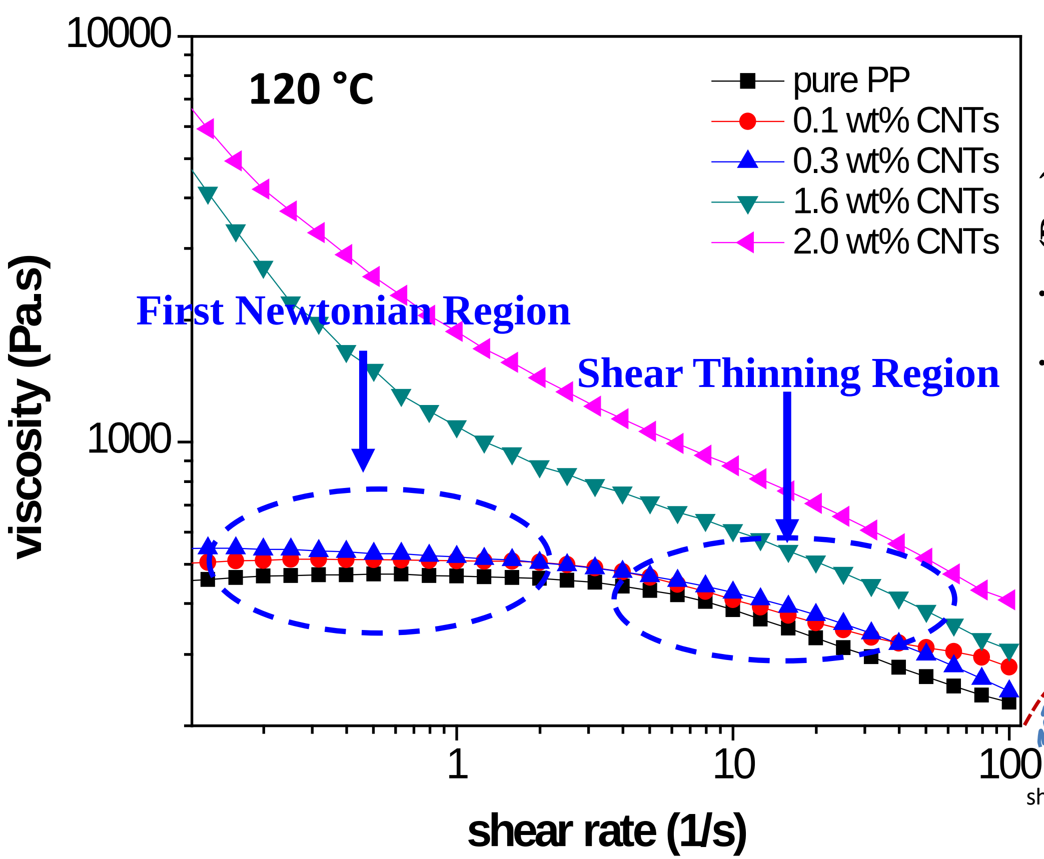
Loading of CNTs	T_c (° C)
Pure PP	113.55
0.1 wt% CNTs	118.64
0.3 wt% CNTs	111.45
1.6 wt% CNTs	103.89
2.0 wt% CNTs	101.59

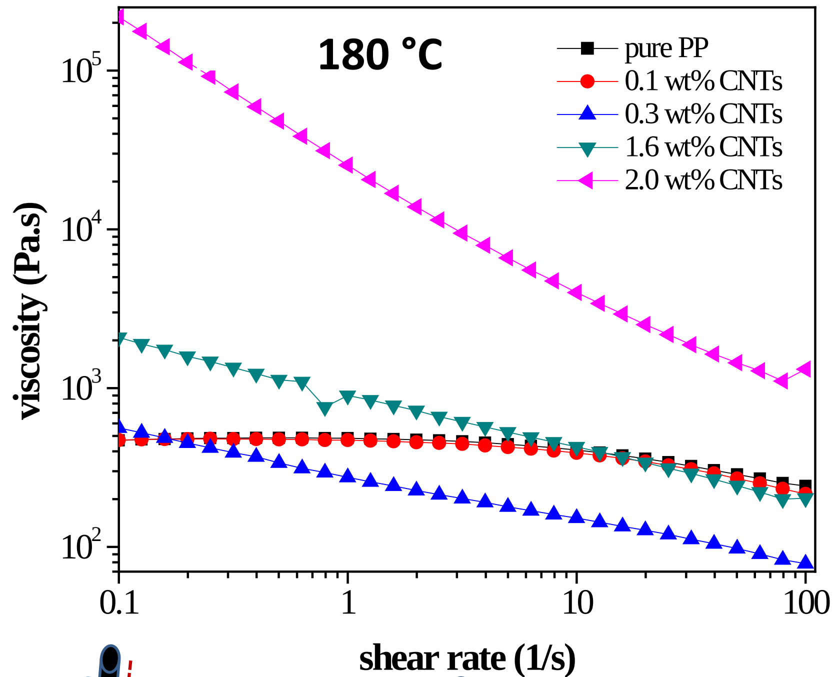
increase

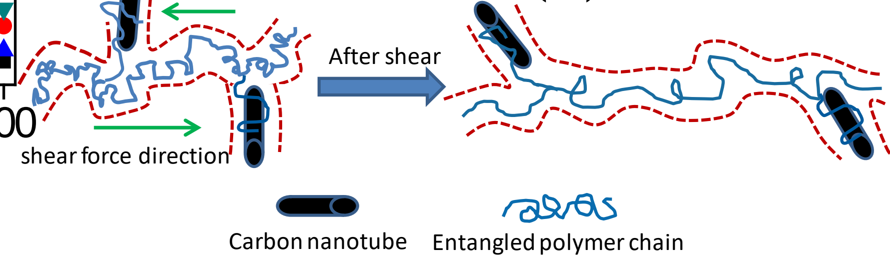
decrease

- **0.1 wt% CNTs would serve as a nucleation and promote the crystallization of PP.**
- **With increasing loading of CNTs, the nanofiller would constrain the movement of the polymer chain.**

Rheological Behavior Study







- **CNTs promote the shear thinning process of PP**
- **CNTs can serve as the branch of the polymer chains**

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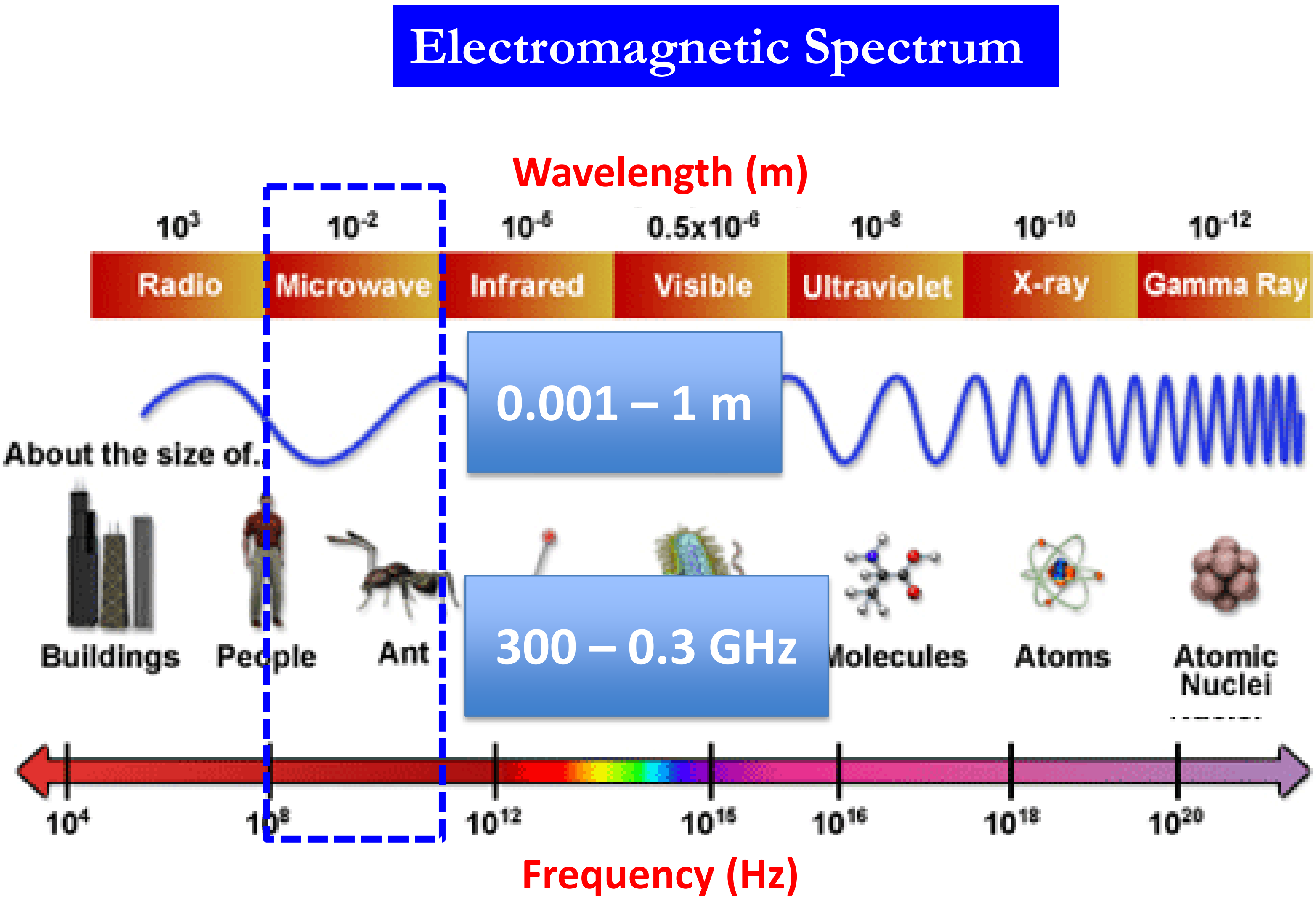
Microwave Radiation

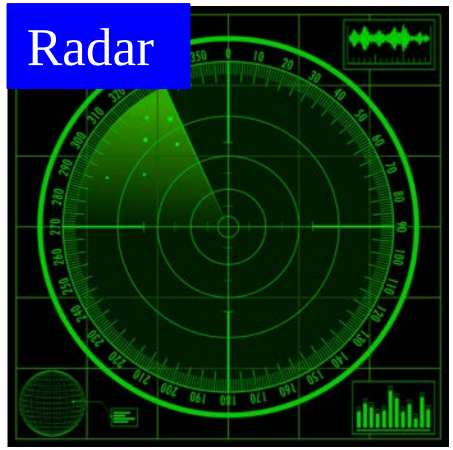


https://nationalmaglab.org/about/around-the-lab/what-the/faraday-cage

Microwave Applications

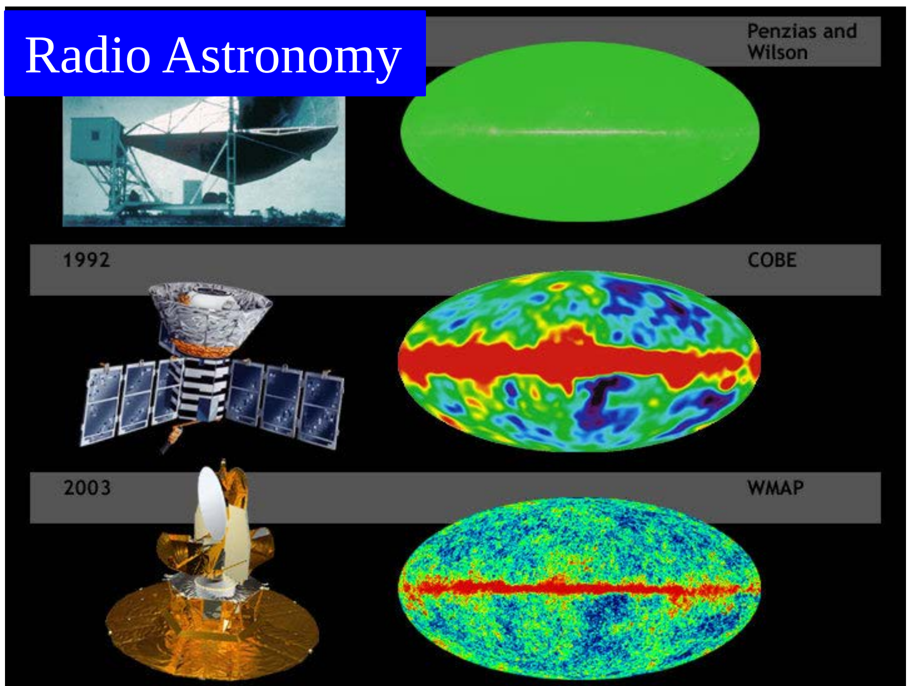
Communications

Radar



Navigation

Radio Astronomy



Heating Resource

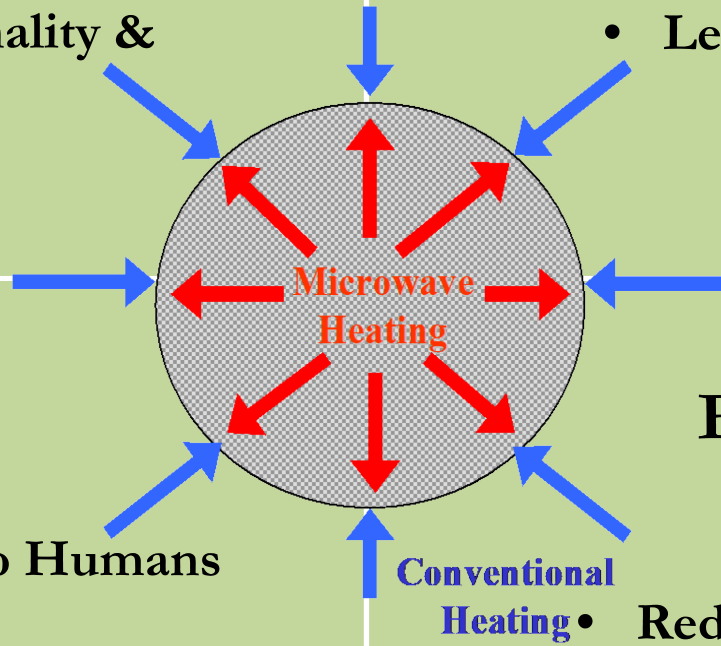
Microwave Heating Advantages

Innovation

- Selective Heating
- Versatile & Scalable
- Enabling Technology to Enhance Functionality & Diversity

Low Waste

- Rapid Energy Deposition
- Reduction of Treatment Cost & Processing Time
- Lean Manufacturing



Healthier

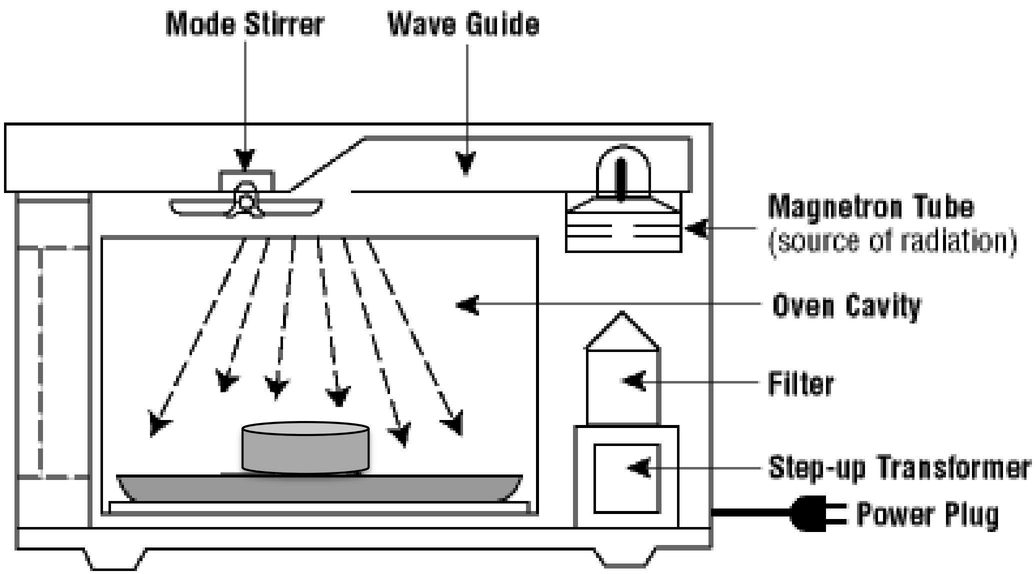
- Reduced Hazards to Humans

Environmental

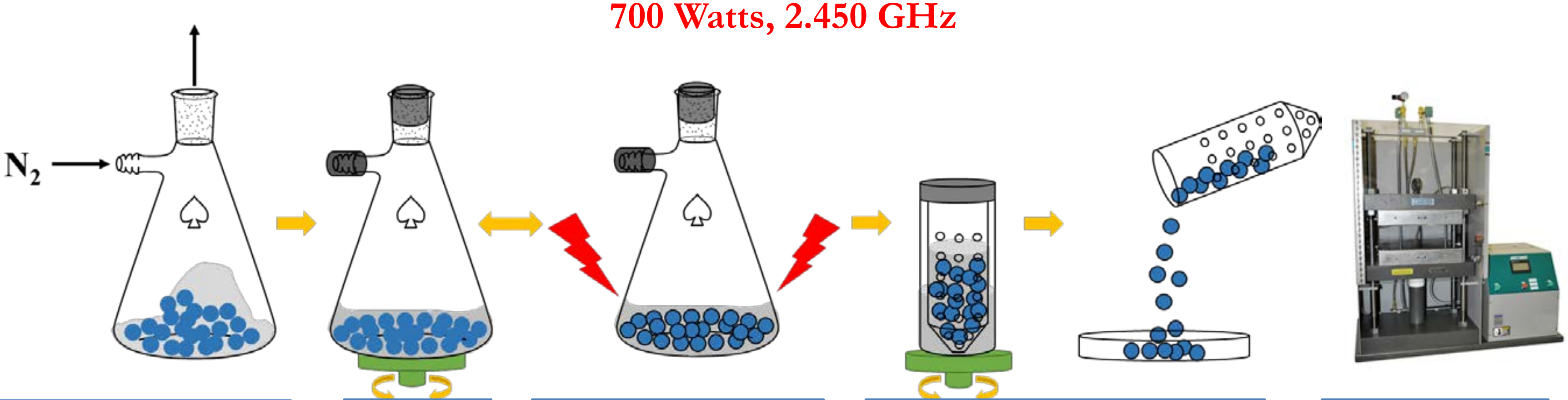
- Renewable
- Reduced Waste & Chemicals
- Energy Efficient

Fabrication Procedure

Materials:
Polypropylene (PP)
$M_w \approx 297\ 000$
Melt flow rate (MFR): 2.0 g 10min^{-1}
Carbon Nanotubes (CNTs)
Average Diameter: 10.4 nm
Average Length: 4.3 µm



700 Watts, 2.450 GHz



5 g PP and 2 g CNTs nitrogen for 15 min

seal shake

5 s as a period shake for 3 s

collect surplus CNTs

140, 160 and 180 °C

4, 5, 6, and 7 periods marked as 20, 25, 30 and 35 s

Formation Mechanism of PP/CNT PNCs

- *Conduction (Joule heating)*
  - **Carbon**
  - **Metal catalyst particles**

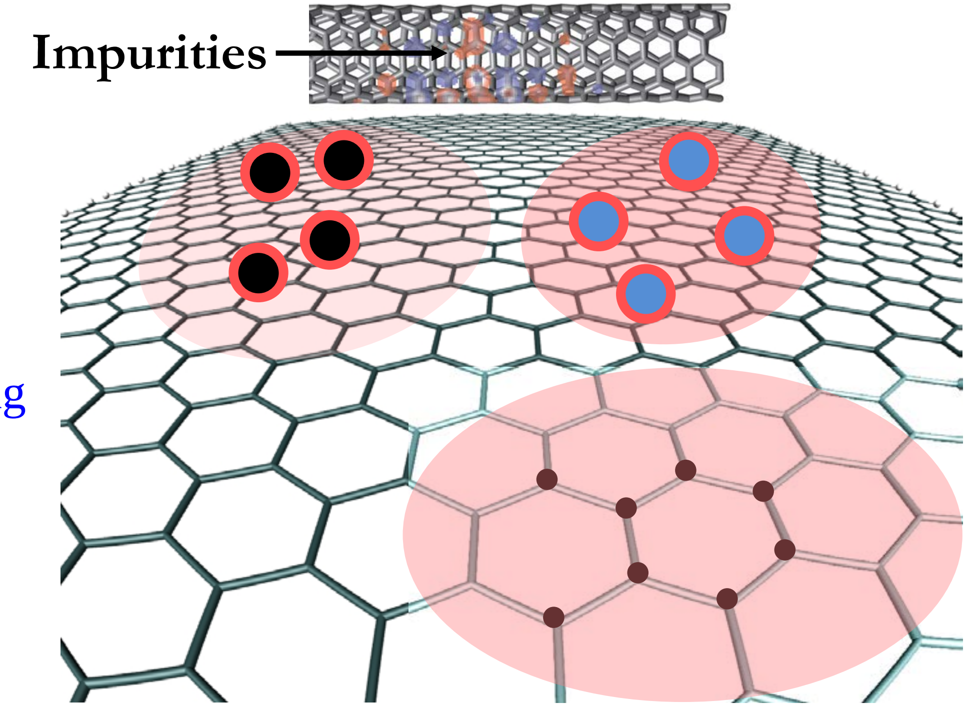
    Motion of the electrons

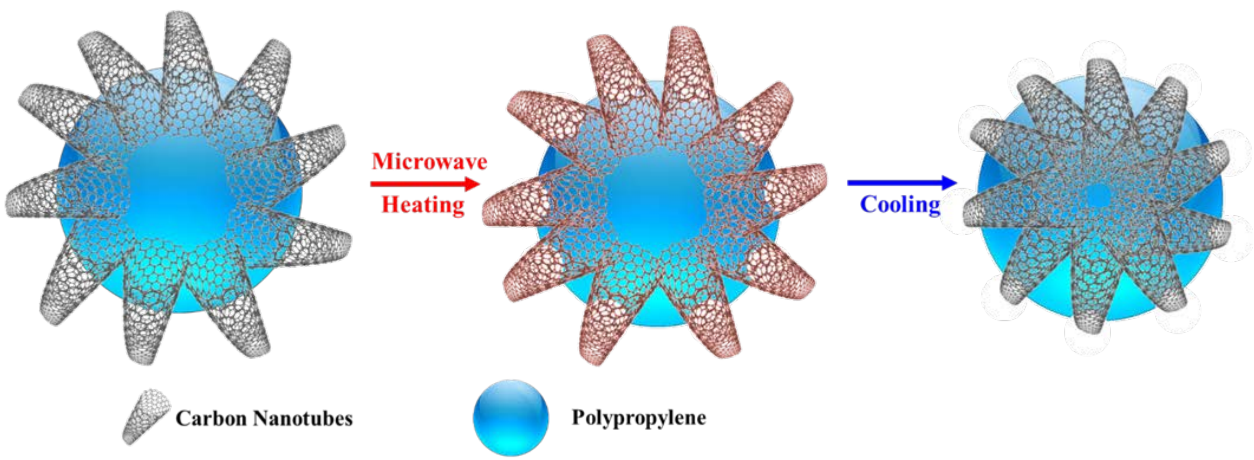
    ↓

    Generation of the localized superheating

- *Polarization*

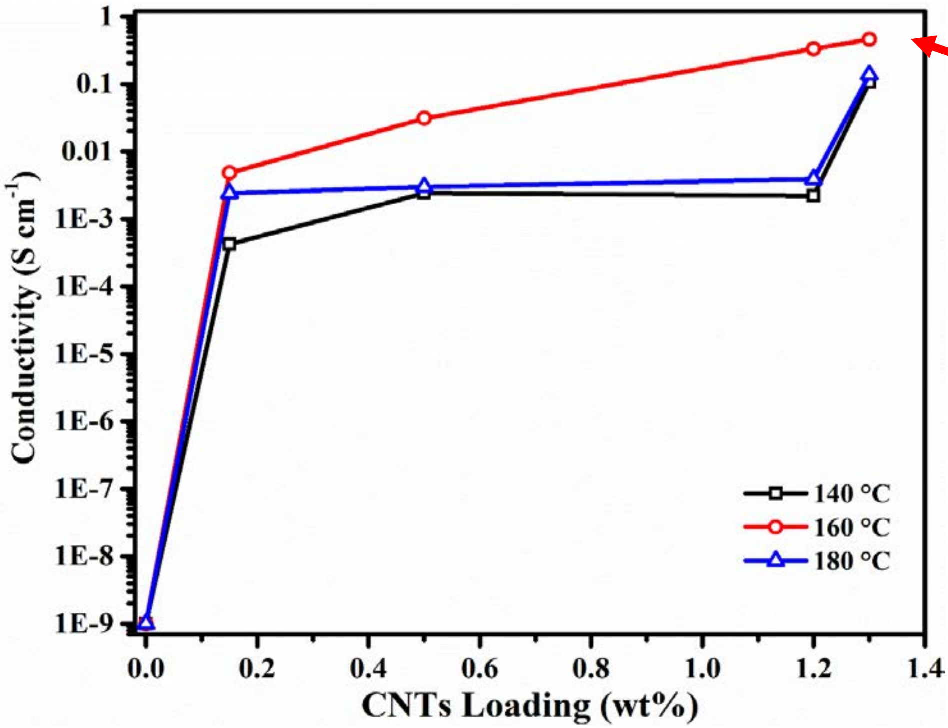
  Transformation of electromagnetic energy into mechanical vibrations

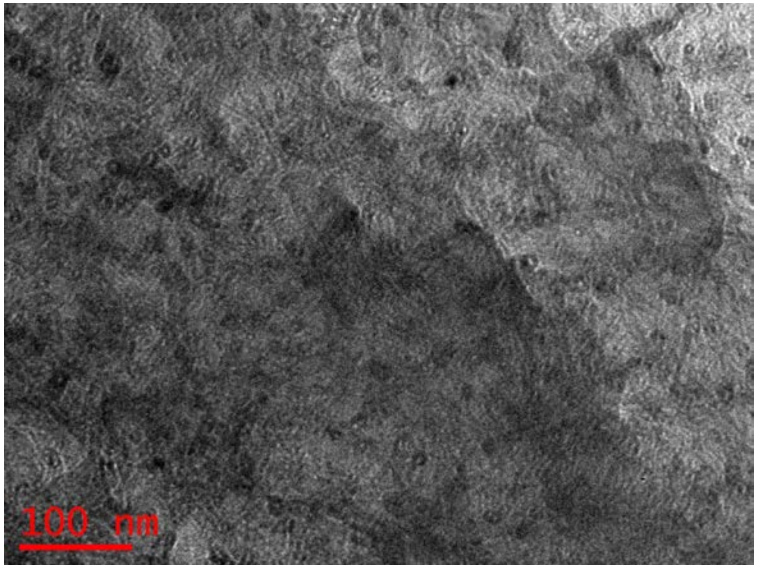


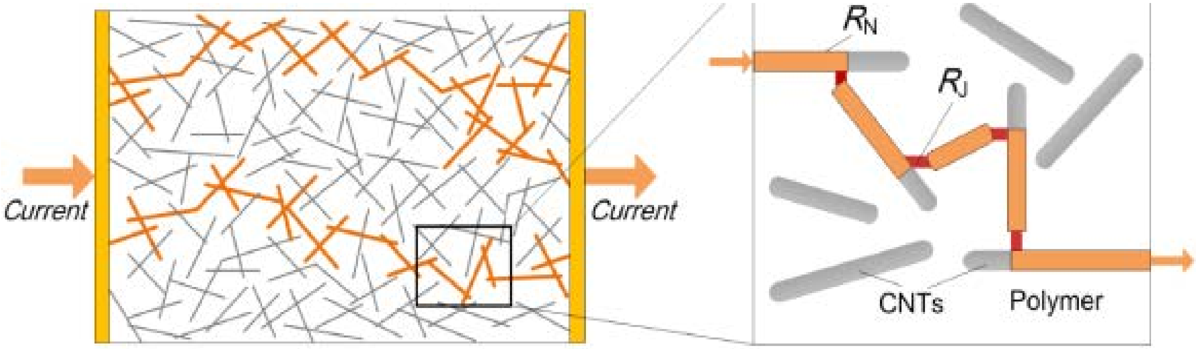


Electrical Conductivity (σ) -- PP/CNTs PNCs

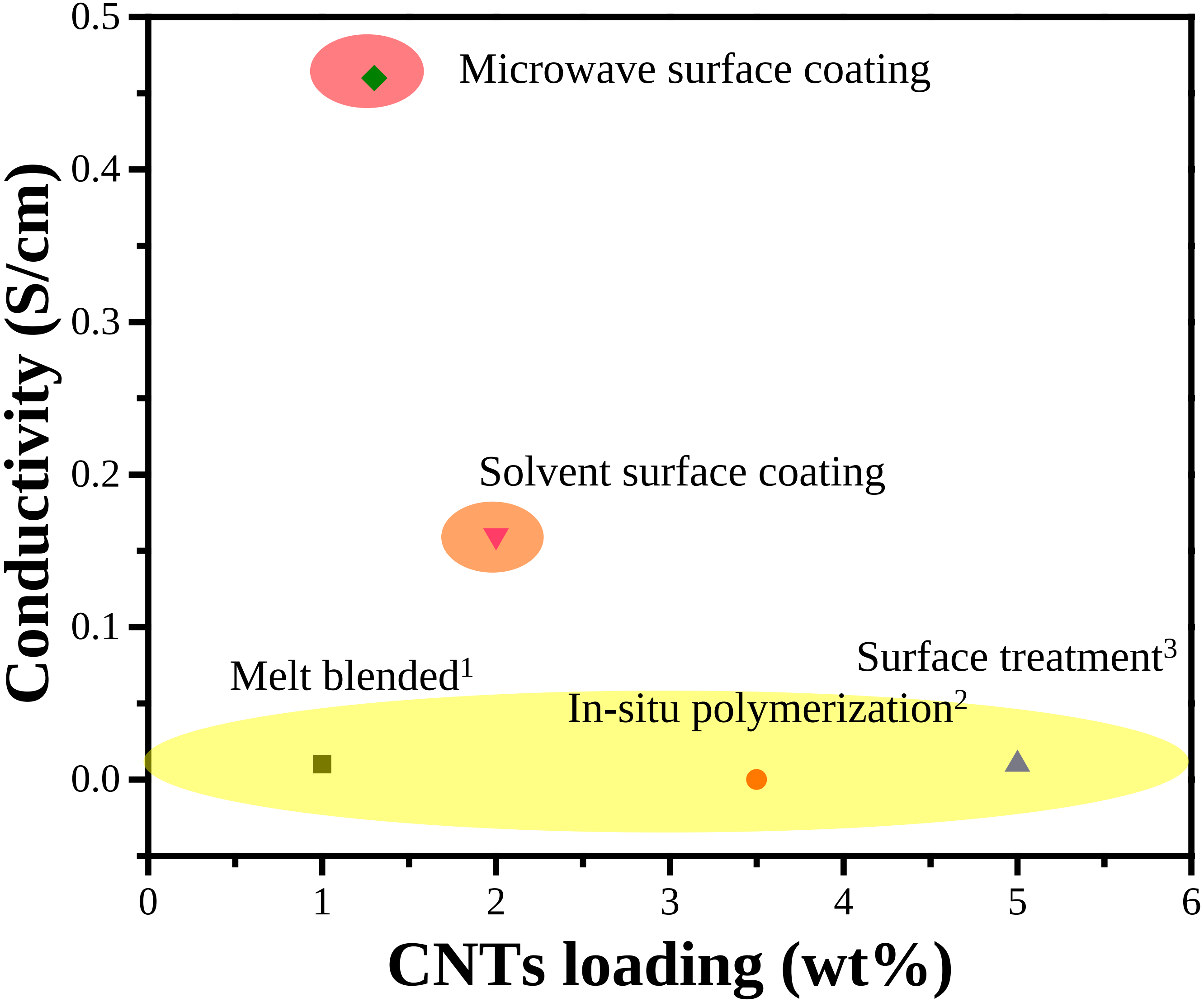
0.46 S/cm





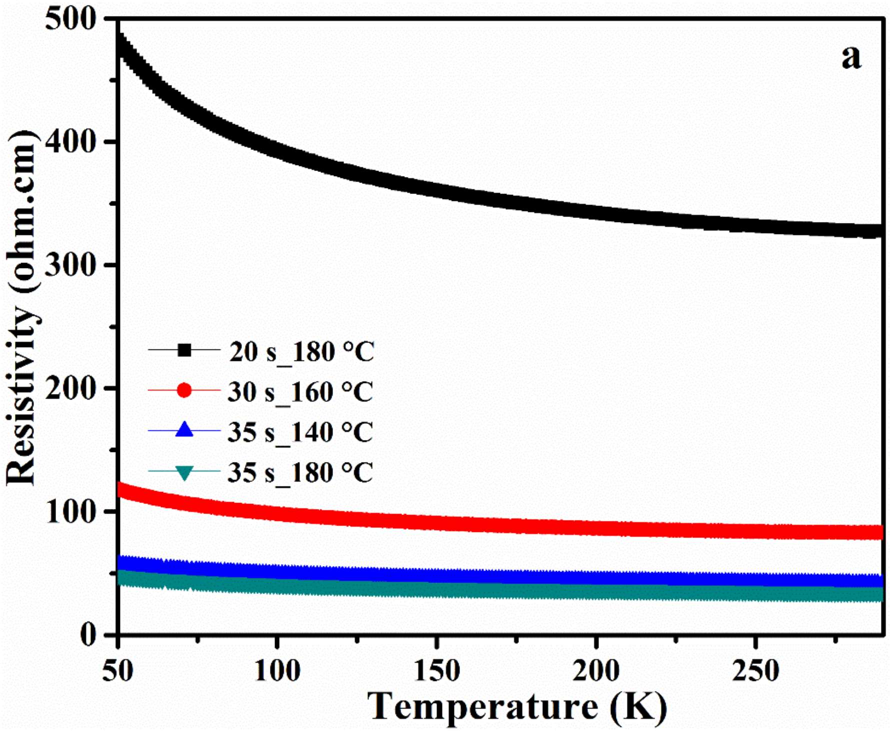


Compare with literature results



1. M. Seo, et al. *Chem. Phys. Lett.*, 2004, 395: 44-48
2. A. Koval'chuk *at al.*, *Macromolecules,* 2008, 41: 3149-3156
3. S. Lee, et al. *Carbon,* 2007, 45: 2810-2822

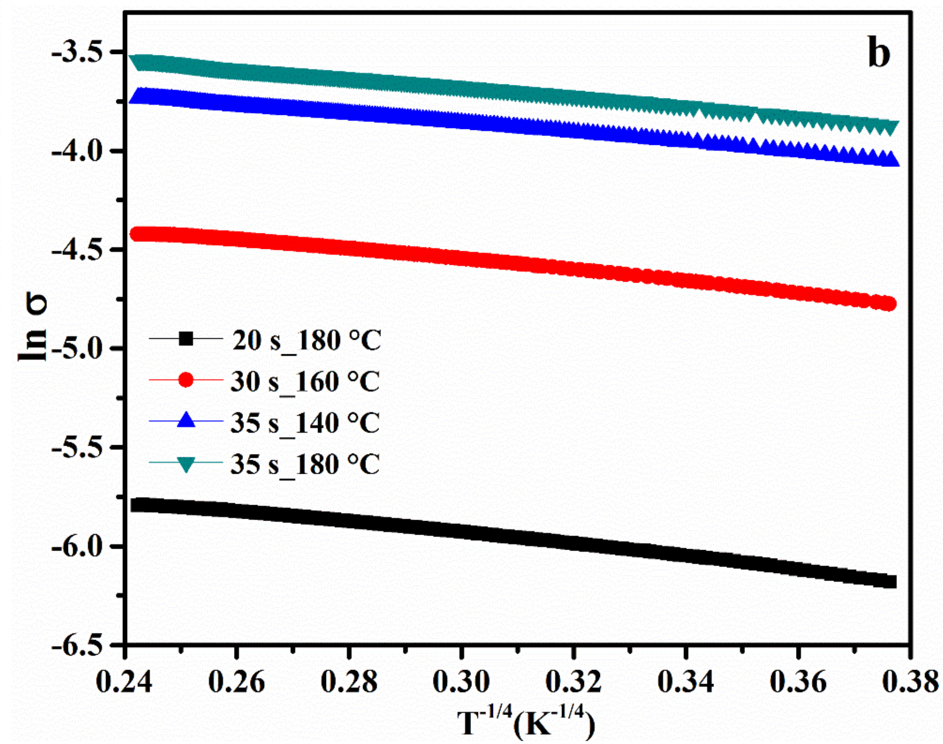
Electron Transport Mechanism



Mott variable range hopping (VRH) approach

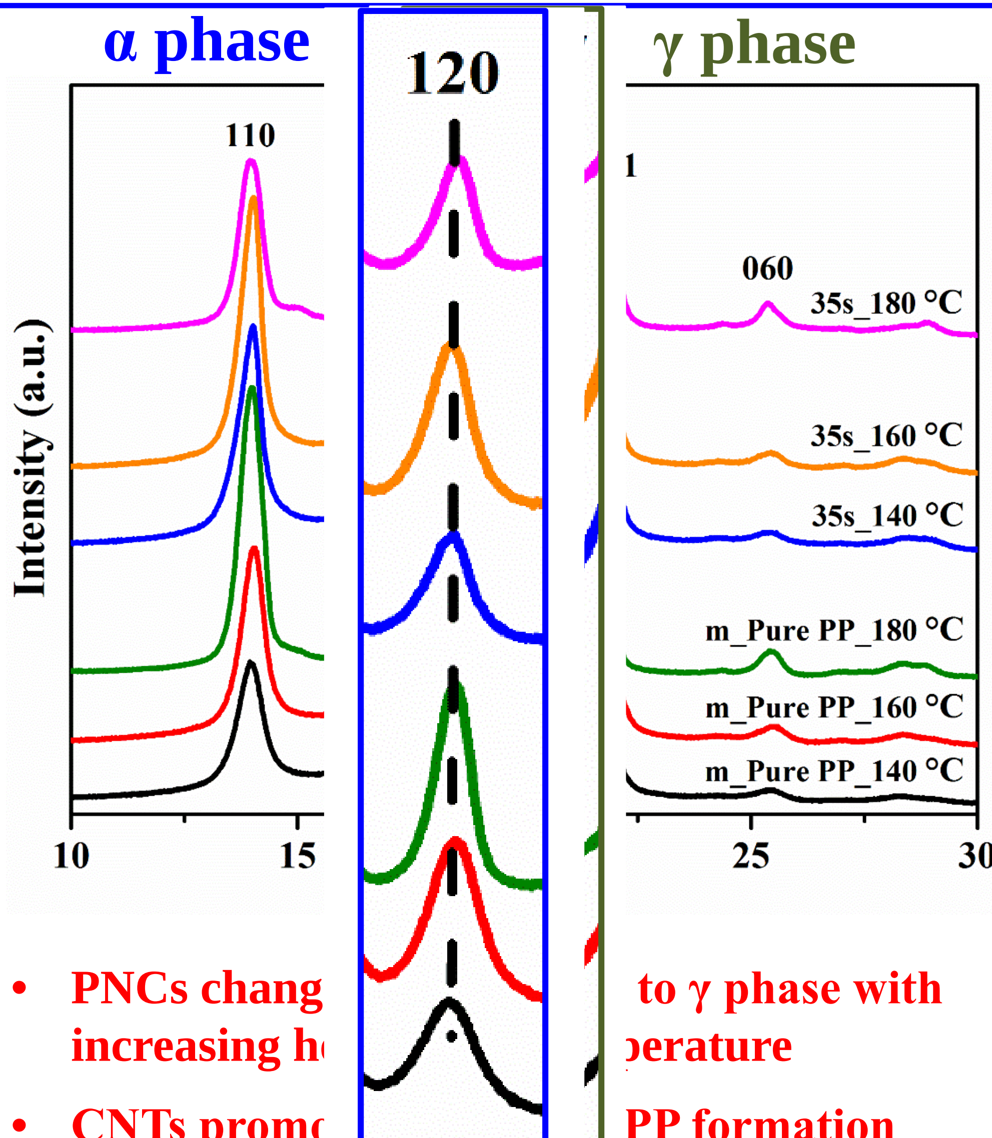
$$\sigma = \sigma_0 \exp[-(\frac{T_0}{T})^{1/(n+1)}]$$

σ_0 : pre-exponential factor, constant;
T_0: hopping barrier



- **Electrical transport mechanism:** *a 3-dimensional variable* range hopping mechanism

Crystal Structure Study



- **PNCs chang... to γ phase with increasing h... perature**
- **CNTs promo... PP formation**

The amount of γ phase PP (X_γ) was calculated[1]:

$$X_\gamma = h_\gamma / (h_\gamma + h_\alpha)$$

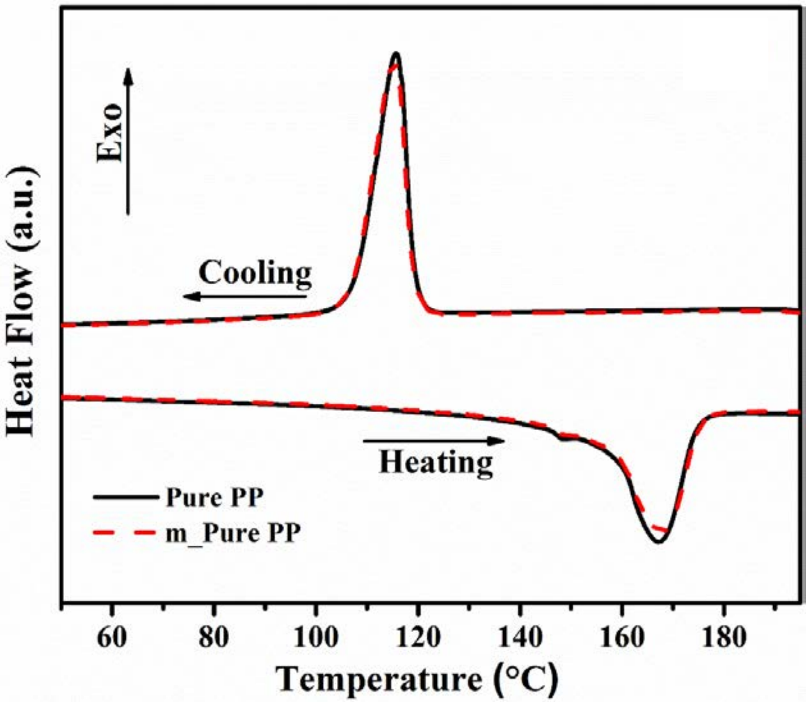
h_γ and h_α are the peak height at 2θ = 20.07 and 18.5° for the (117) and (131) peak, respectively.

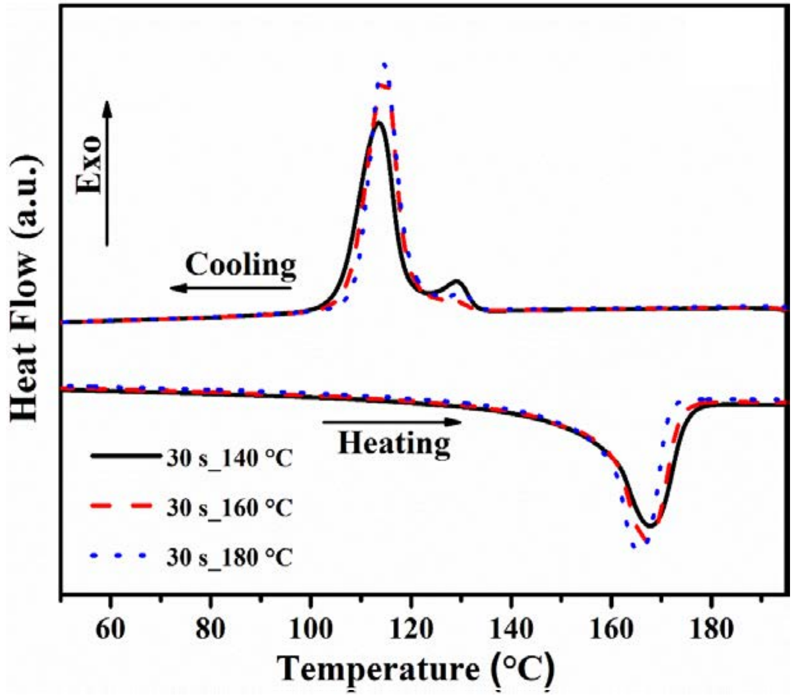
Amount of γ phase PP

Samples	180 °C
Pure PP	0.1197
1.3 wt% CNTs	0.3676

1. Thomann; Wang; Kressler; MÃlhaupt, Macromolecules, 29, 8425-8434 (1996)

Crystallization Study





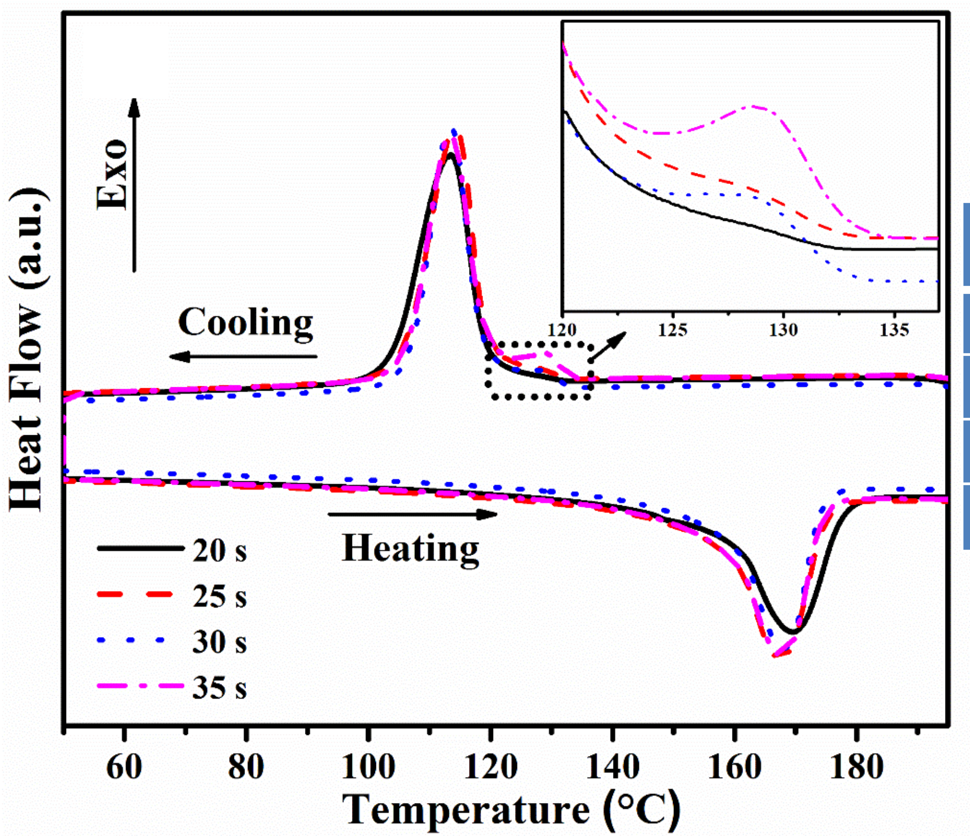
Treatment Time	T_c (°C)	ΔH_c (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	F_c (%)
Pure PP	115.71	154.0	167.33	124.2	59.43
m_Pure PP	115.19	154.2	167.70	124.0	59.33
30 s_140°C	113.55	151.4	167.81	127.6	61.79
30 s_160°C	114.69	152.9	167.22	129.3	62.62
30 s_180°C	114.70	153.6	165.59	129.4	62.67

- **Microwave has no influence on pure PP**
- **Higher process temperature promotes the crystalline structure formation of the PP chains**

T_c crystalline peak temperature ΔH_c enthalpy of the crystallization F_c crystalline fraction

T_m melting peak temperature ΔH_m enthalpy of the fusion

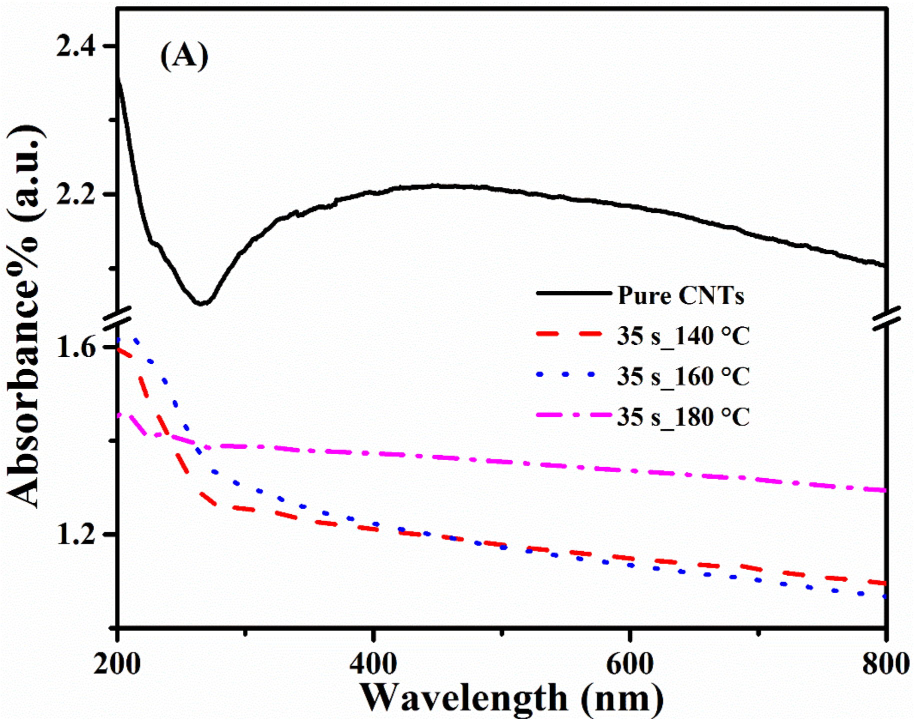
Crystallization Study



Treatment Time	T_c (°C)	ΔH_c (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	F_c (%)
20 s	113.38	151.0	169.45	130.6	62.58
25 s	114.29	150.7	168.55	131.0	62.99
30 s	113.36	150.2	168.14	132.1	63.97
35 s	113.29	151.8	167.88	133.8	64.86

- **Both α and γ phases of PP were formed during crystallization**
- **CNTs can serve as nucleation sites and foster the crystallization of PP**

Optical Property Study

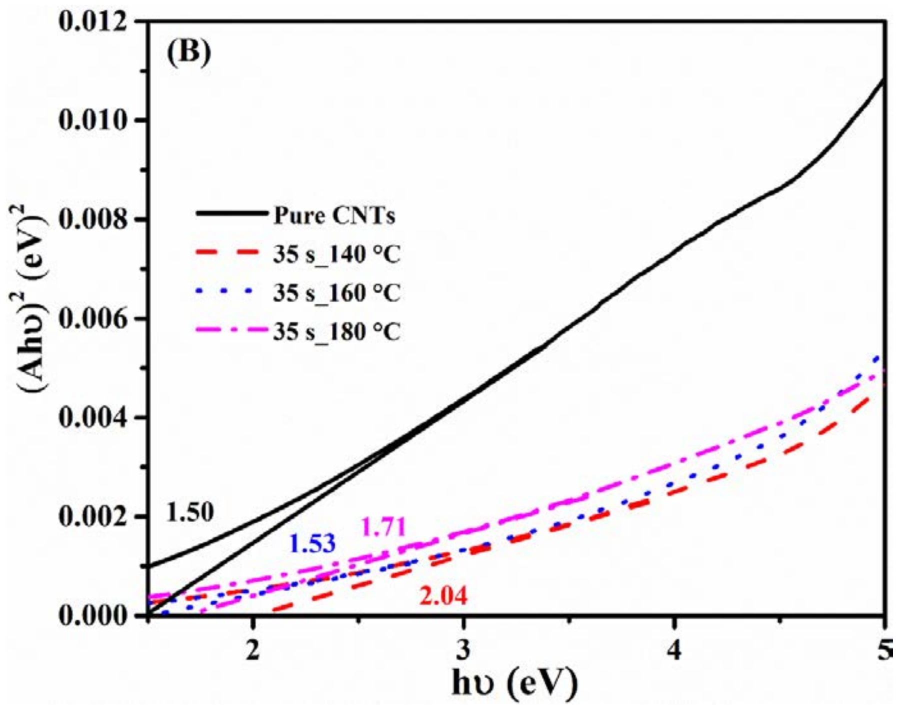


The photonic energy band gap value of the CNTs was obtained from the Tauc plot[1]:

$$\alpha h\upsilon = (h\upsilon - E_g)^n$$

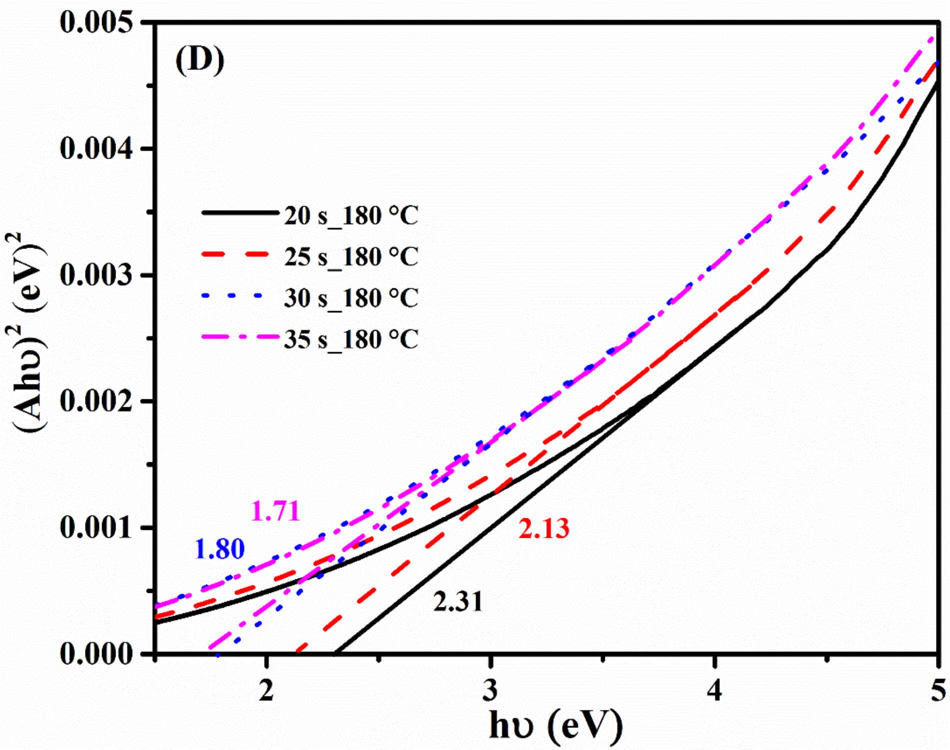
α absorbance coefficient
h planck constant
υ photon frequency
E_g the photonic energy band gap

n is a pure number associated with the different types of electronic transitions: n is 1/2 for direct-allowed and is 2 for indirect-allowed.



1. Tauc, Mater. Res. Bull., 5, (8), 721-729 (1970)

Optical Property Study



PNCs	E_g /eV
20 s_180 ºC	2.31
25 s_180 ºC	2.13
30 s_180 ºC	1.80
35 s_180 ºC	1.71

- **Band gap decrease with increasing loading of CNTs.**
- **The changing tendency is in good agreement with the conductivity result.**

Outline

- Introduction
- Research Work

  Part I: Solvent Surface Coating Method

  Part II: Microwave Radiation Surface Coating Method
- **Conclusions**
- Acknowledgement

Summary

❖ **CNTs can promote γ phase PP formation in the PNCs.**

❖ **At lower loading (0.1 wt%), the CNTs would serve as nucleation sites of PP and promote the crystallization by reducing the surface free energy barrier towards nucleation.**

❖ **CNTs can serve as the branch of the polymer chains and favor the disentanglement of polymer chains.**

❖ **Well-formed CNTs network resulted in higher electrical conductivity and the electrical conductivity mechanism stayed within a 3 dimension variable range hopping.**

❖ **The changing trend of Eg value of the PNCs followed the electrical conductivity value of PNCs, representing the PNCs with higher conductivity showed a lower Eg.**

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Acknowledgement

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THANK YOU !

Questions

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