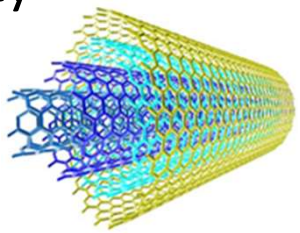
Microwave Characterization of Multi Walled Carbon Nanotubes Polymer Composites

Dr. Muna HajjYahya
AL – Najah National University
Physics Department

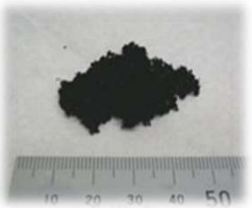
Research Activity Context

Benefits of CNTs to polymers

- Increase of Electrical conductivity
- Improvement of mechanical properties, especially strength



- Enhancement thermal stability and conductivity



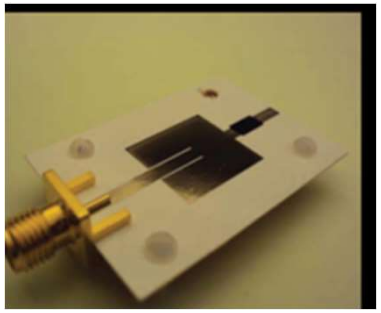
High aspect ratio → Effects at low CNT contents < 5wt.%

MWCNTs polymer composites → Many microwave applications

Involved

Potential Application Fields of CNTs

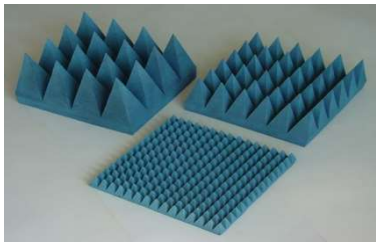
GROWING INTEREST IN NEW MATERIALS FOR:



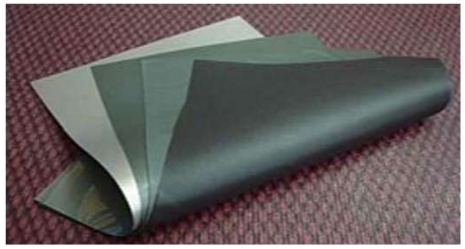
Antennas Design

Car enamel

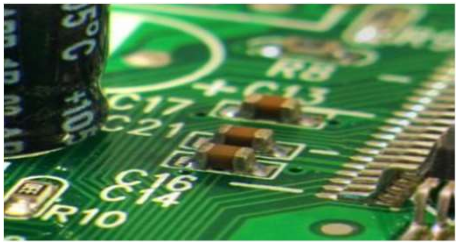
Electromagnetic Shielding



Radar Adsorbing Material (RAM)



Satellite and automotive applications



Capacitors (charge storage)

Objectives of the Research Activity

Nanocomposites preparation

Goals:

- **To obtain a good dispersion**

DC conductivity measurements

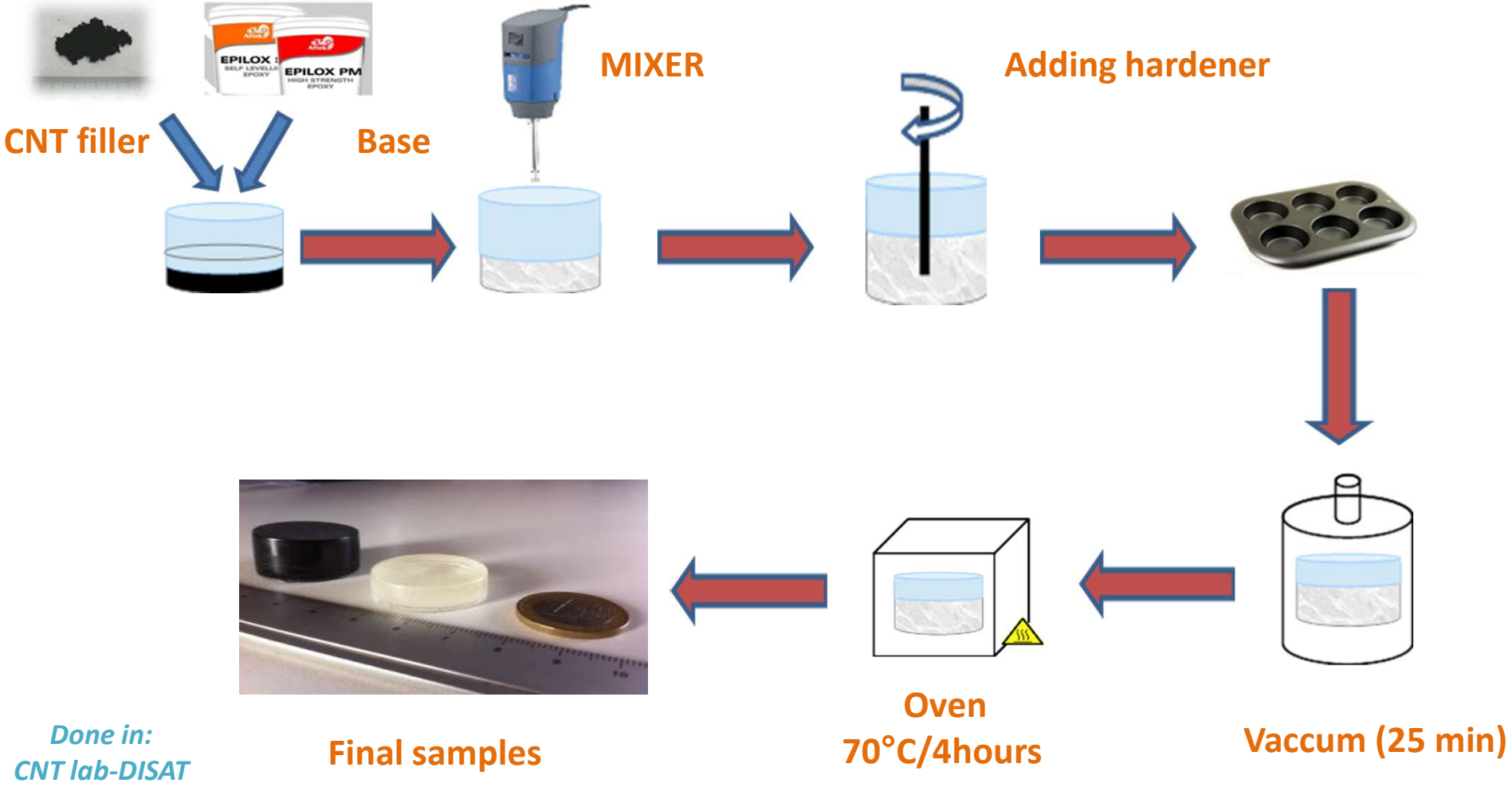
- **Percolation threshold of MWCNTs**

Complex permittivity measurements

Goals:

- **Measure the complex permittivity with:**
  - **Small samples**
  - **Wide freqency band**
  - **Easy and fast method**
- **Statistical analysis indipendence of the samples**

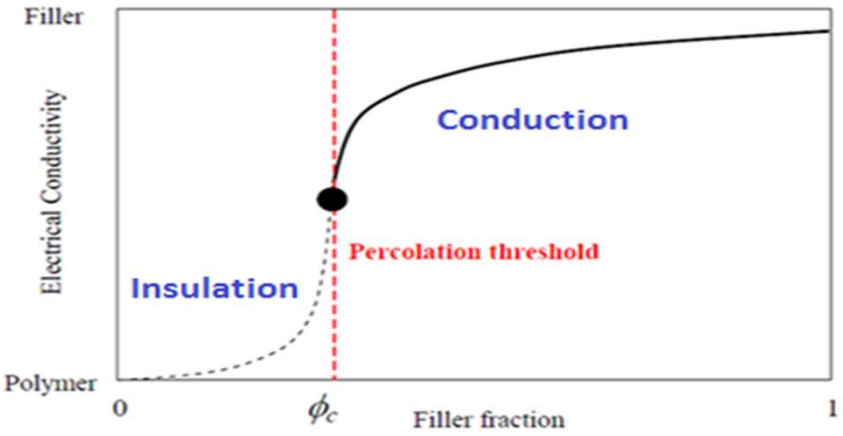
Nanocomposites Preparation - Polymer Based MWCNTs Reinforced Composites Preparation Procedure



Nanocomposites Preparation - Types of Multi-Walled Carbon Nanotubes Used

Acronym	Type	Diameter [nm]	Length [µm]	Aspect Ratio (AR) (Length/ Diameter)	Producer	Purity (weight %)
MW0	Short Multi Wall	30 – 50	0.5 – 2	17 - 40	Cheaptubes	> 95
MW3	Short Thin Multi Wall	9.5	1.5	150	Nanocyl	> 95
MWG-1	Graphitized MW	20-30	10-30	500 - 1000	Cheaptubes	>99.5
F4	-COOH Functional MW	9.5	1.5	150	Nanocyl	> 95
E15	Multi Wall	25 – 45	> 10	200 - 400	Nanothinx	=98.5
E16	Multi Wall	6 – 10	> 10	1000 - 1600	Nanothinx	>90
MW6	Multi Wall	18-35	> 10	285 - 555	Nanothinx	97

Percolation Threshold of MWCNTs



The most widely used definition is

$$P_c = \frac{1}{AR}$$

Other formulas for evaluating percolation threshold :

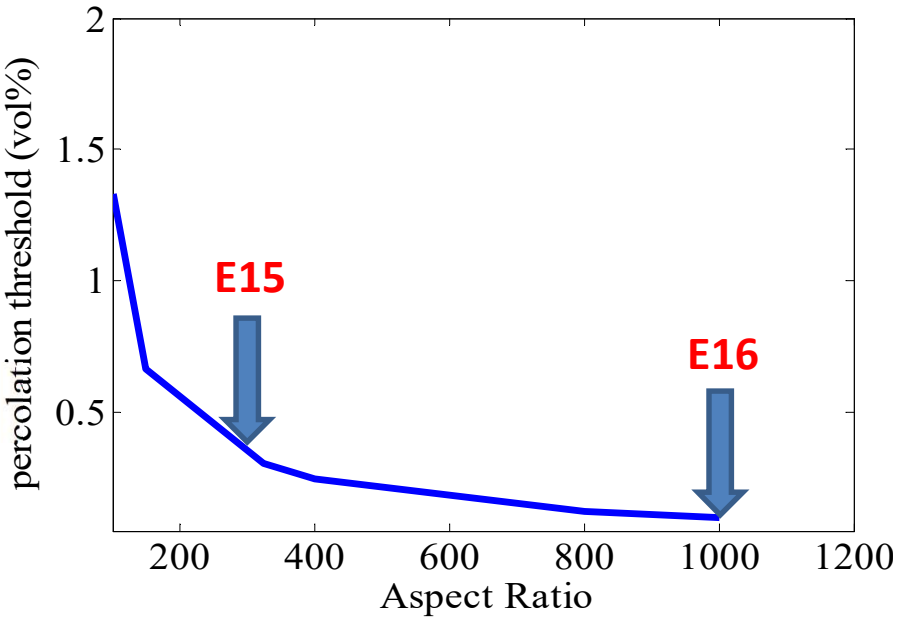
$$P_c = \frac{1}{2AR} \qquad P_c = \frac{0.7}{AR}$$

When CNT Vol % > Pc ⇒ Reaching conductive behavior

- Bauhofer W, Kovacs JZ: A review and analysis of electrical percolation in carbon nanotube polymer composites. *Compos Sci Technol* 2009, 69:1486–1498.
- Balberg I, Anderson CH, Alexander S, Wagner N. Excluded volume and its relation to the onset of percolation. Phys Rev B 1984;30(7):3933-43.
- Celzard A, McRae E, Deleuze C, Dufort M, Furdin G, Marêchê JF. Critical concentration in percolating systems containing a high-aspect-ratio filler. Phys Rev B 1996;53(10):6209-14.

Nanotubes can be conducting or insulating depending on their properties:

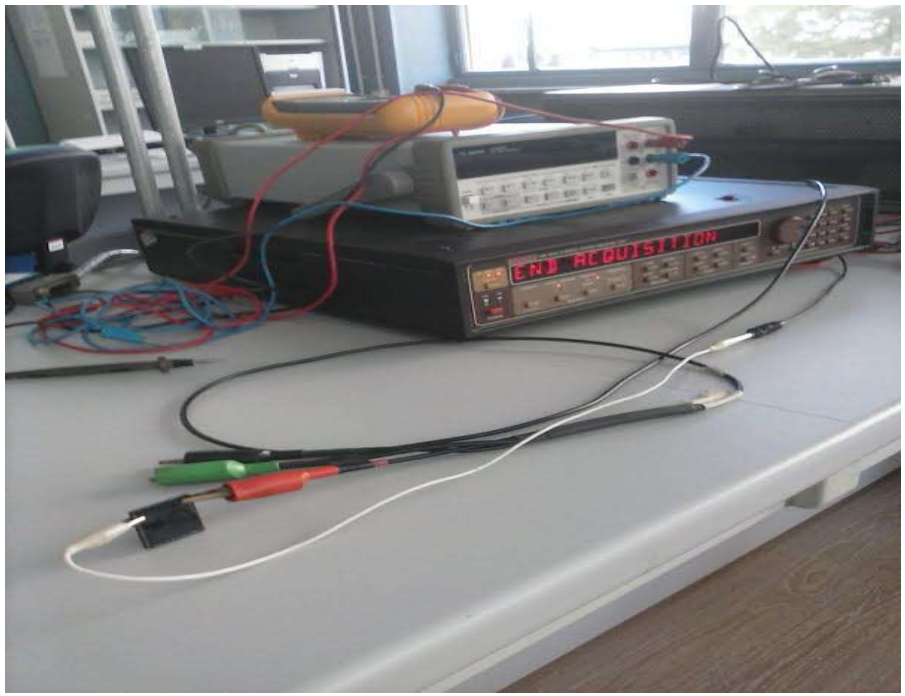
- **Diameter**
- **Length**
- **Chirality/twist**
- **Number of walls**



Resistance Measurements

A two point probe (TPP) method

- **Stable electrical contact**
- **Using A Keithley-238 High Current Source**



Goals:

- **Average value for the resistance**
- **Test sample uniformity**

In cooperation with:
Mauro Giorcelli

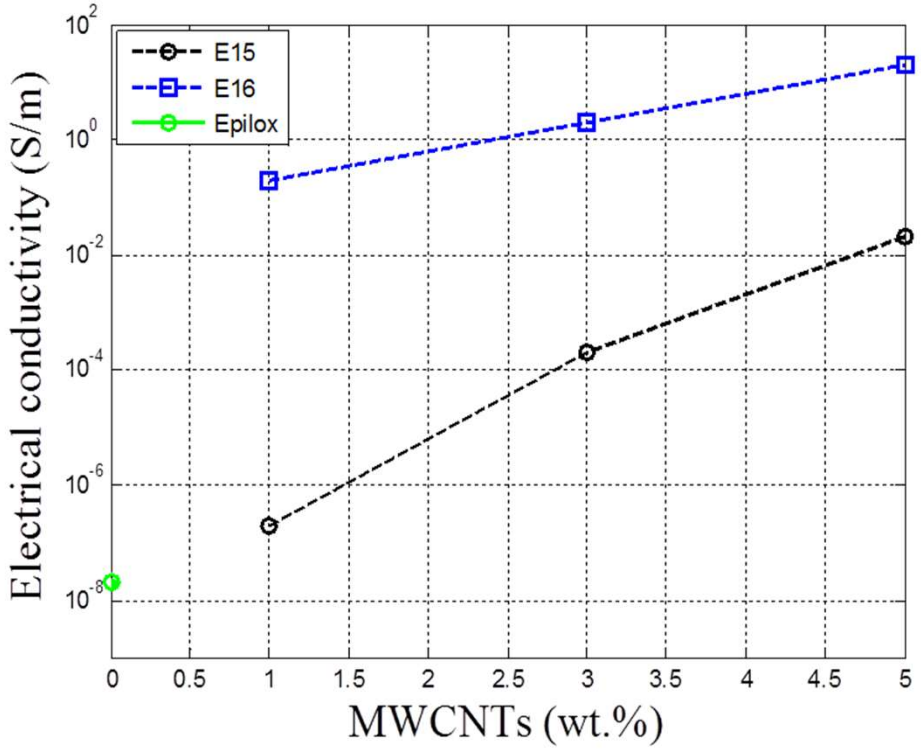
DC Conductivity

Electrical conductivity:

$$\sigma = \frac{I}{V}\frac{l}{A}$$

Higher aspect ration → Higher conductivity

Increasing wt.% → Conductivity increasing



CNTs type	Diameter [nm]	Length [µm]	Aspect ratio	Density (g/cm^3)
E15	25 - 45	>10	200 - 400	2.05
E16	6 - 10	>10	1000 - 1600	2.12

Permittivity Measurements Setup

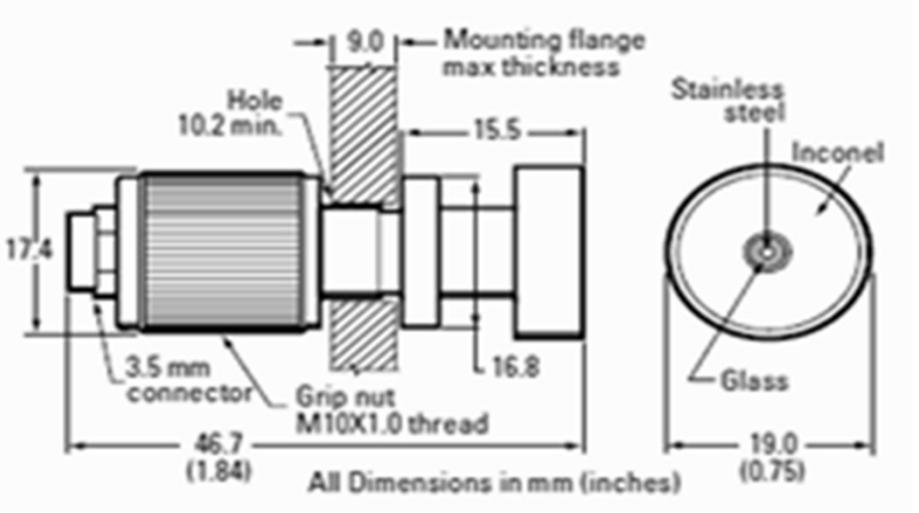
A Network Analyzer (E8361A) + A commercial dielectric probe (Agilent 85070D)

Advantages:

- ☺ Frequency band 200 MHz – 20 GHz
- ☺ Fast response
- ☺ Samples of small dimensions

Drawback:

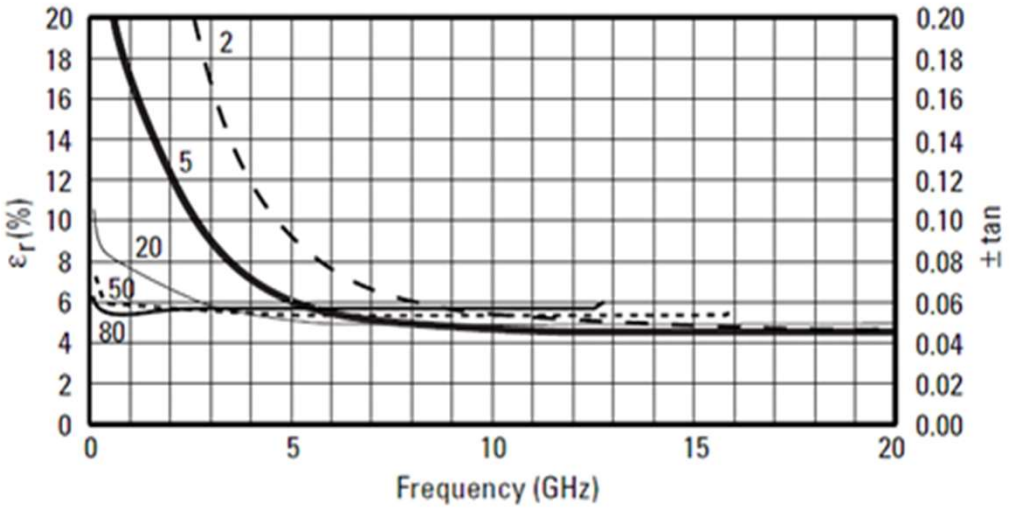
- ☹ Roughness and flatness of the surface are critical
- ☹ Thick samples



A commercial dielectric probe (Agilent 85070D)

Performance Characteristics of Dielectric Probe

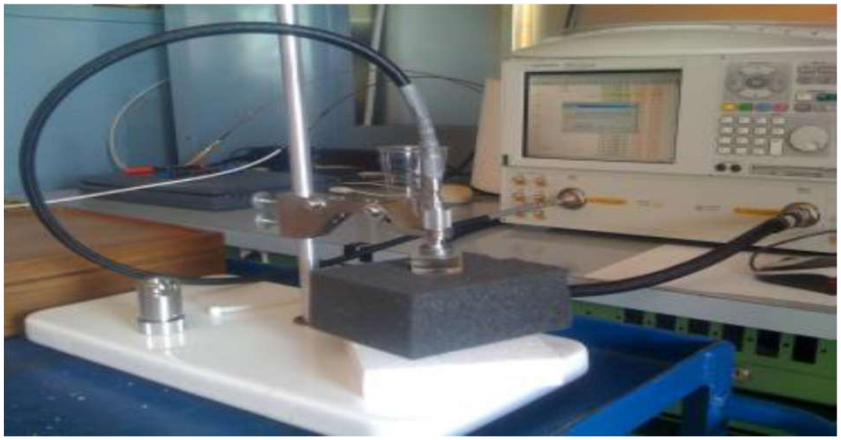
Frequency range	200MHz - 20GHz (nominal)
Temperature	-40°C to 200°C
Homogeneity	The sample should be homogeneous
Surface roughness	The sample should be flat
Diameter of sample	>20 nm
Thickness of sample	$> \frac{20}{\sqrt{\varepsilon_r}}$ nm
Granule size	< 0.3 mm
Maximum recommended ε_r	<100
Minimum recommended $tan\delta$	>0.05
Accuracy in real permittivity	±5%
Accuracy in $tan\delta$	±5%



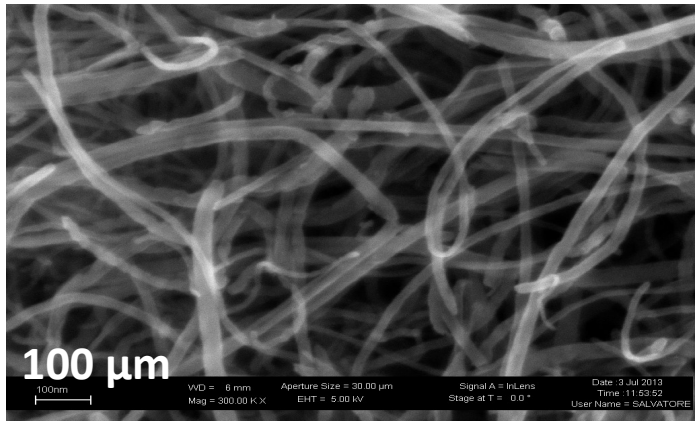
Calibration

→ Air\Short\Water

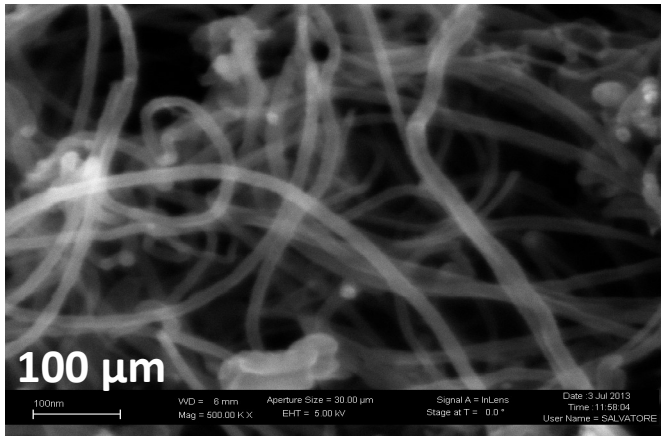
→ Removing systematic errors



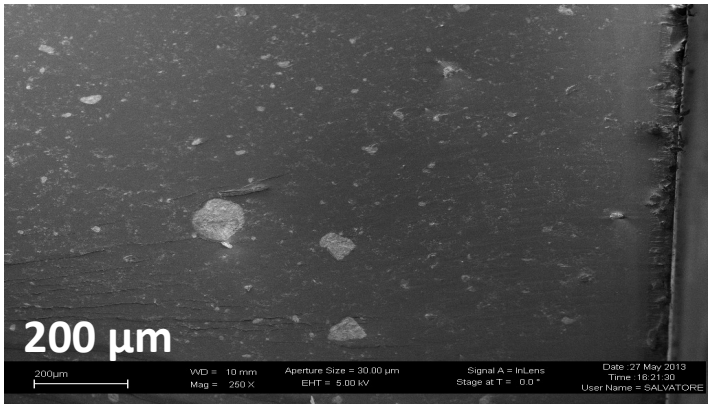
FESEM Analysis



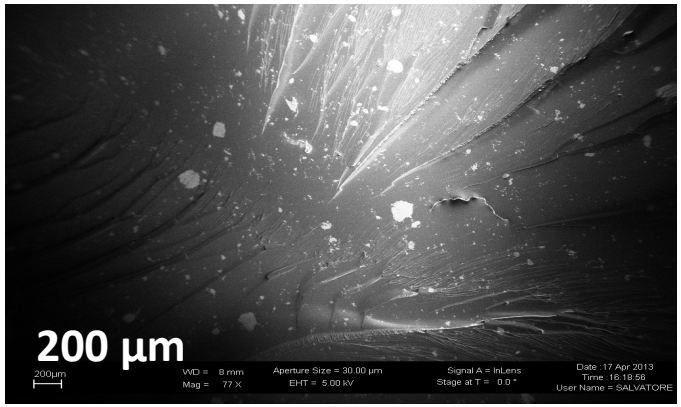
E15 material



E16 material



Crio-fractured E15 surface of composite

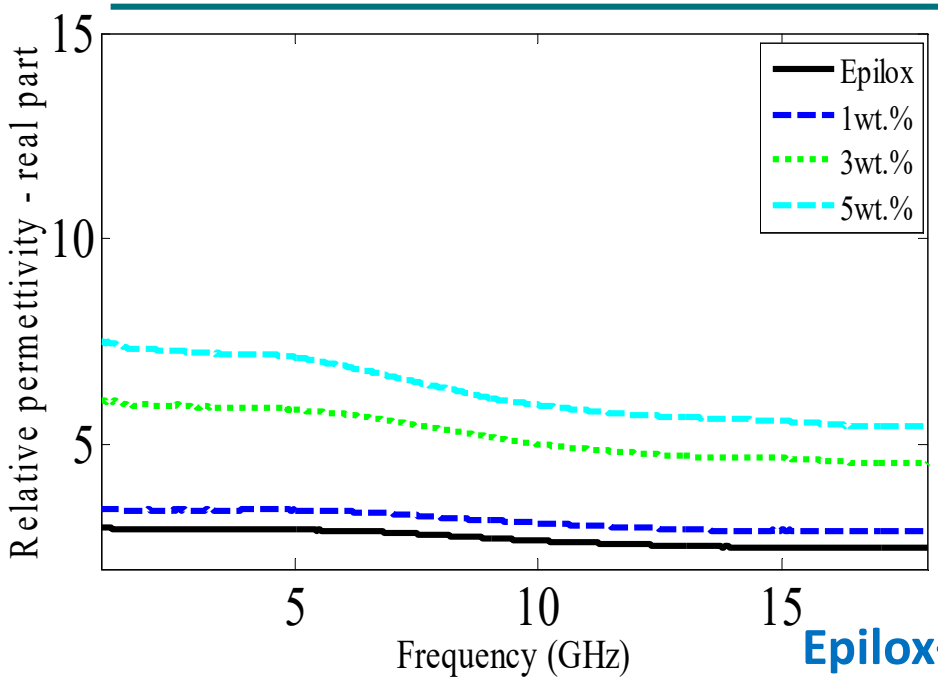


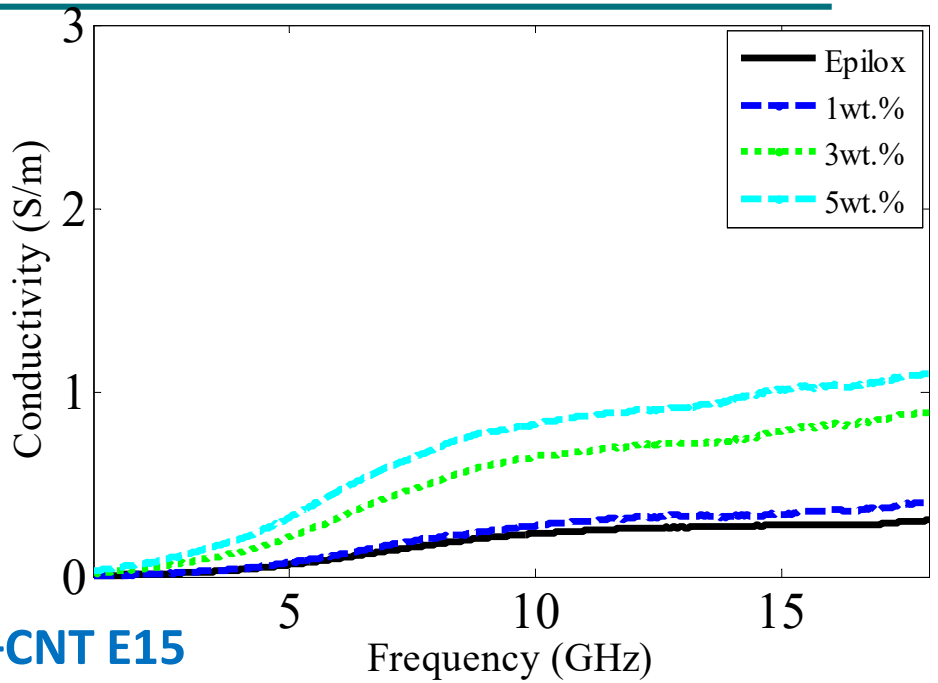
Crio-fractured E16 surface of composite

Done by :
Salvatore Guastella – DISAT Department

FESEM: Field Emission Scanning Electron Microscopy

Investigation on the Effects of Increasing of CNT Loading





Epilox+CNT E15

E15

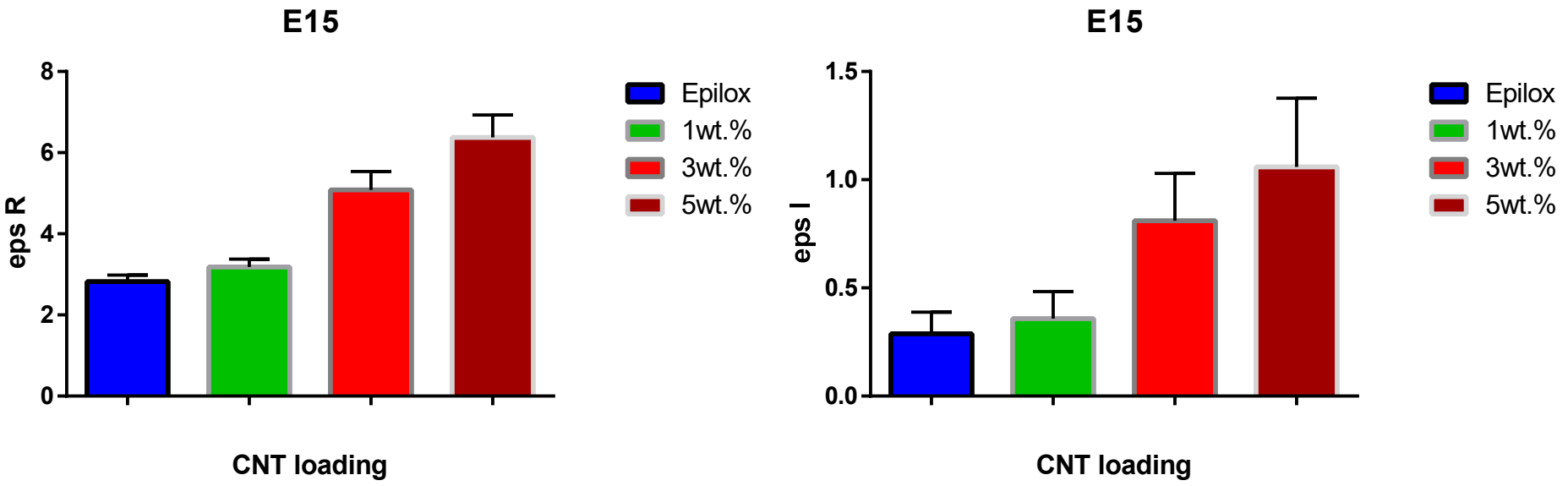
Increasing wt% →
- Permittivity increase
- AC conductivity increase

All the volume fractions used of E15 > Pc **BUT** good results starts from 3wt.% (1.92vol.%)

E15-1wt.% (0.64 vol.%) results approximately the same of Epilox **BECAUSE OF** Problems in Dispersion of prepared composites and existence of bubbles .

Diameter [nm]	25 – 45
Length [µm]	>10
Aspect ratio	200 - 400
Density (g/cm^3)	2.05
Pc	0.1 vol.%

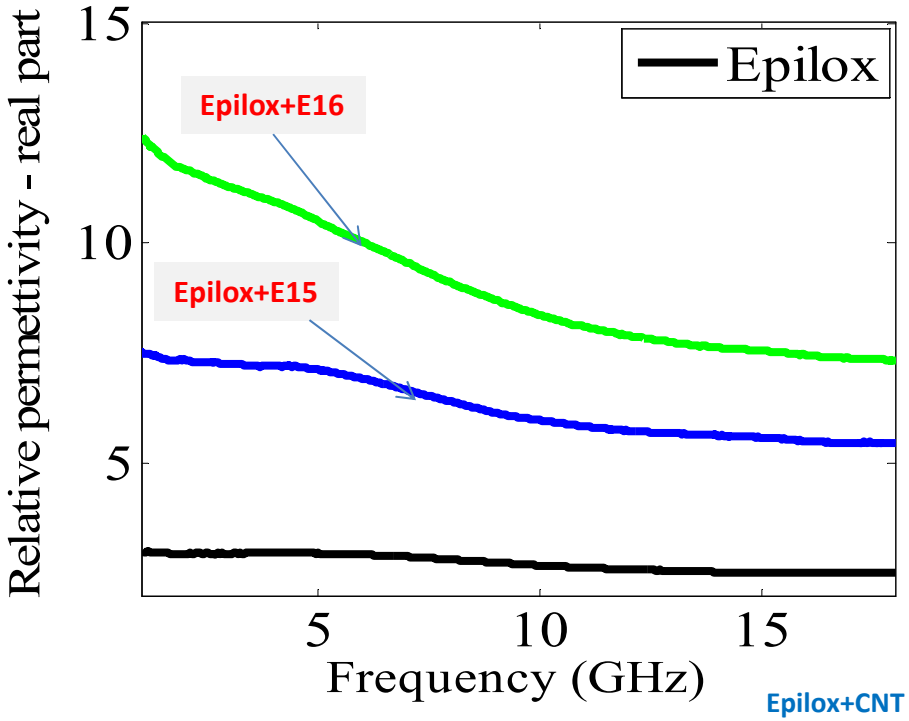
Statistical Analysis

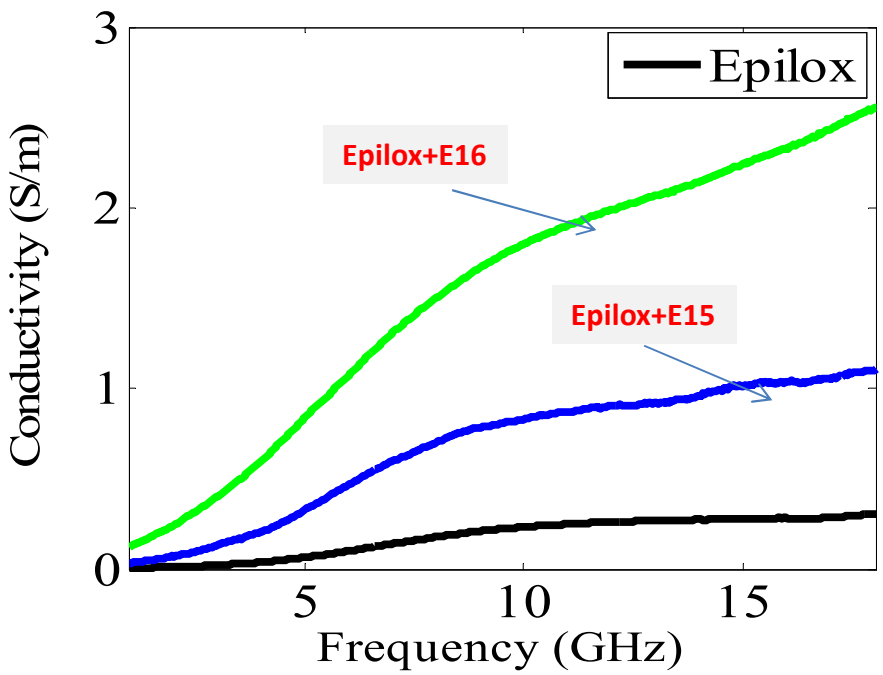


Comparing E15 - 1 wt.% samples to Epilox → The variation is not significant

Increasing the CNT concentration → Imaginary permittivity increase → Electrical conductivity increase

Comparison of Different Types of CNT with Different Aspect Ratio





Epilox+CNT E15-5wt.%
Epilox+CNT E16-5wt.%
} comparison

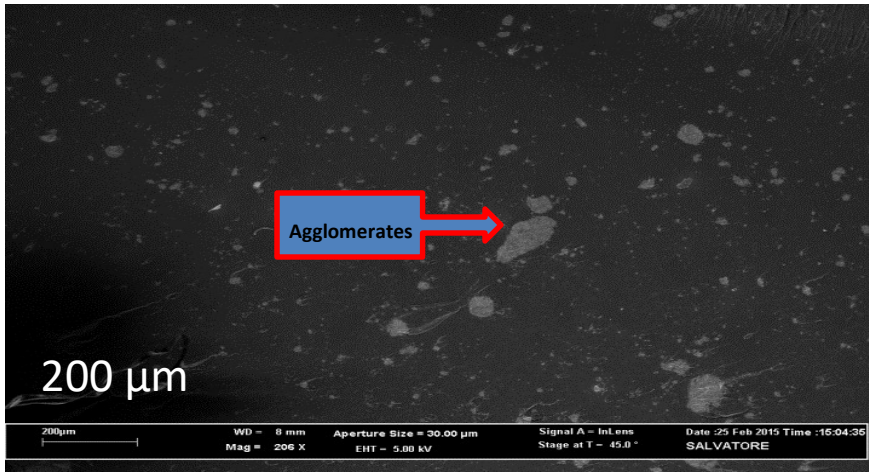
- **Number of walls**
- **Aspect Ratio**
- **Desnity**

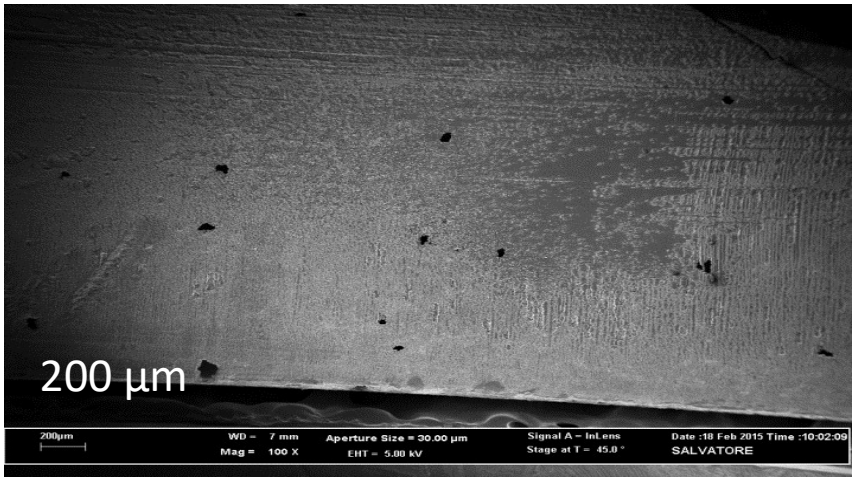
→ **Play an important role**

CNTs type	Diameter [nm]	Length [µm]	Aspect ratio	Density (g/cm^3)
E15	25 - 45	>10	200 -400	2.05
E16	6 - 10	>10	1000 - 1600	2.12

Analysis of Dispersion of Nano-fillers in Polymer Matrix

FESEM analysis – two mixing procedures





By: Ultra turrax

By: Three roll mills

Epilox+CNT MW6 – 1wt.%

Three roll mills mixing → **Better dispersion of nano-fillers in polymer matrix**

MW6

Diameter [nm]	18 - 35
Length [µm]	>10
Aspect ratio	285 - 555

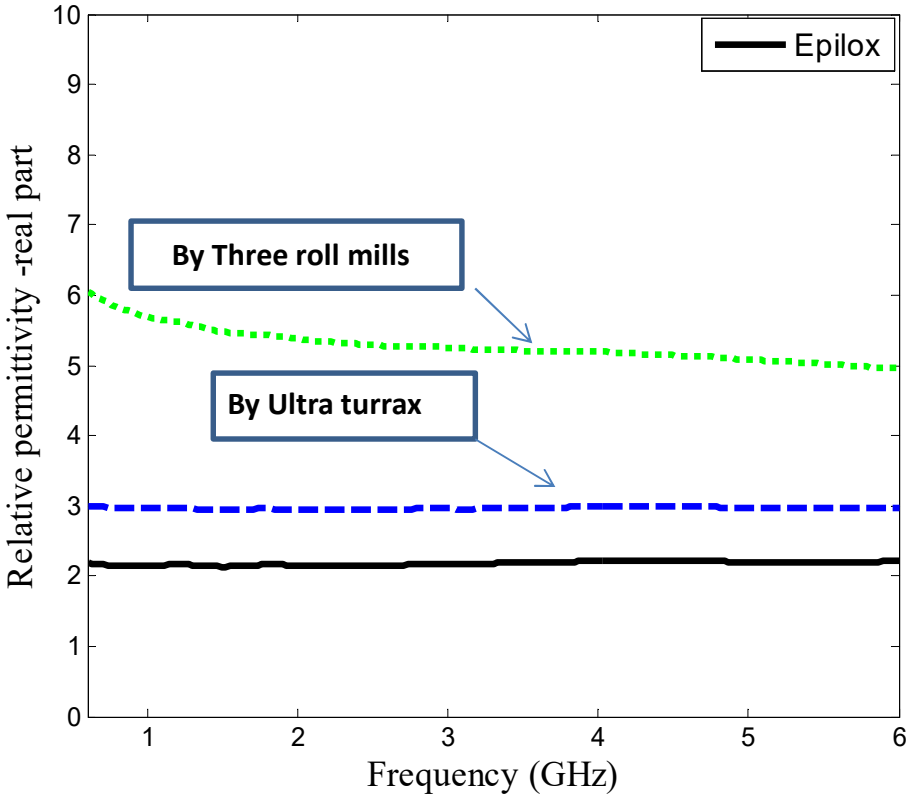
Done by:
Salvatore Guastella – DISAT Department

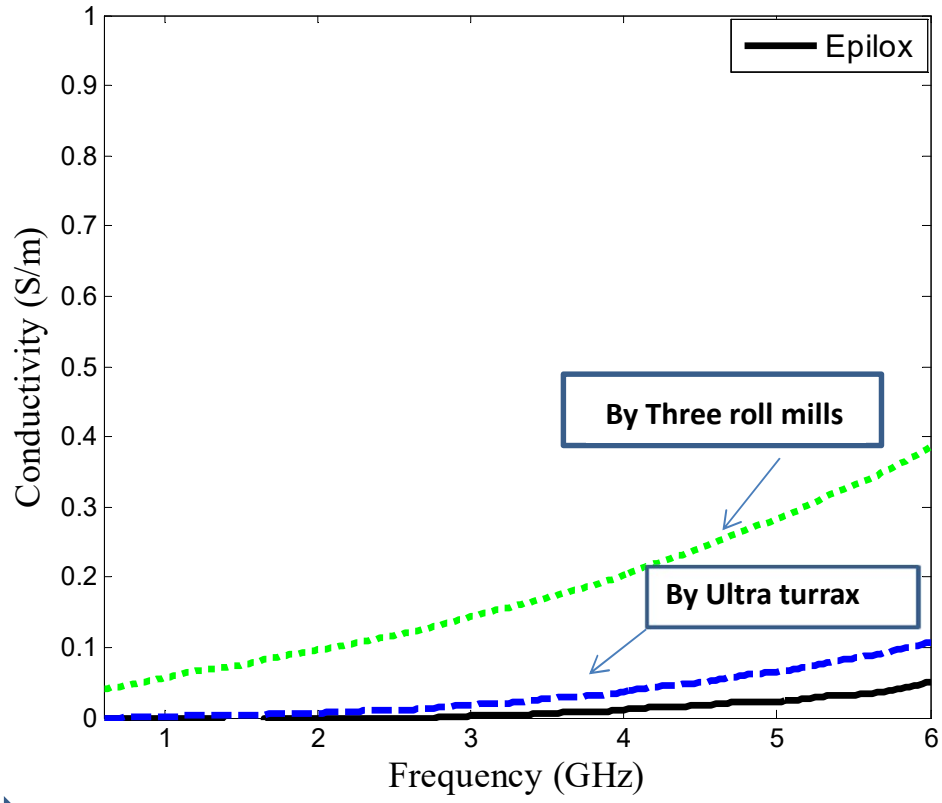
FESEM: Field Emission Scanning Electron Microscopy

Analysis of Dispersion of Nano-fillers in Polymer Matrix

Complex permittivity - two mixing procedures

Epilox+CNT MW6 – 1wt.%





Three roll mills mixing procedure

Higher permittivity and AC conductivity

Thanks for Your Attention