Radiation processed conducting polymer nanocomposites for artificial skin applications

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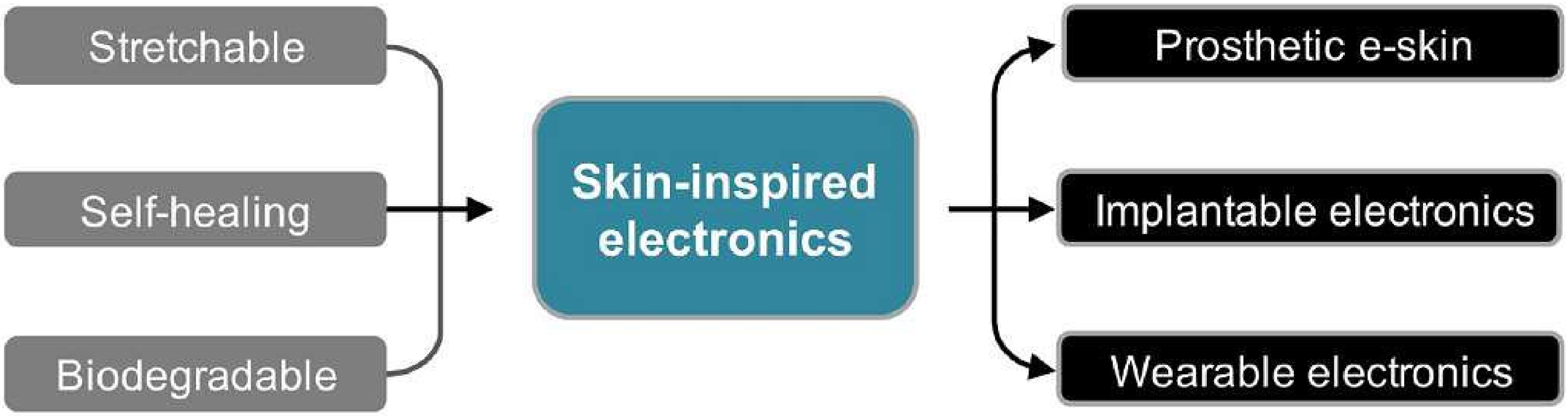
Layout

- **Introduction**
  (materials for artificial skin, properties, components..)
- **Conducting polymer nanocomposites for piezoresistive sensors**
- **Radiation processing of polymers for engineering the microstructure**
- **Our study on radiation processed PDMS and carbon filler based nanocomposites**
- **Summary**

Artificial Skin

Integrating functions of skin into electronic devices

New generation of materials with skin-like properties

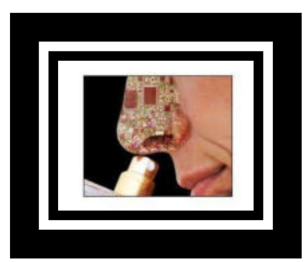


Biocompatibility

Wang et al. Acc. Chem. Res. (2018)

Mechanoreceptors
Thermoreceptors
Chemoreceptors
Sensors…….

Robotic Arm



Artificial Nose

Skin: tactile sensor

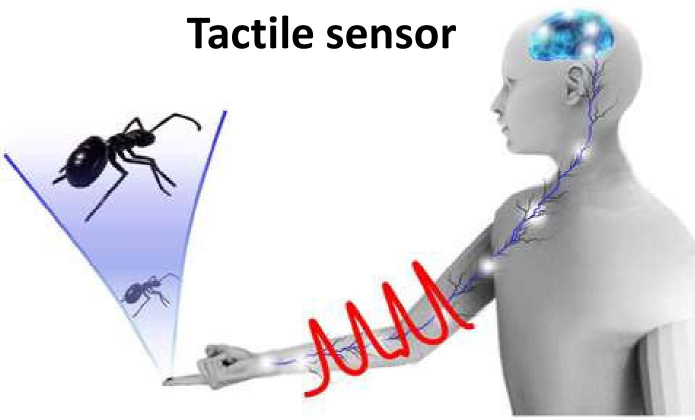
Artificial Tongue

Courtesy: wikipedia

Artificial /e-skin: Sensing the Senses

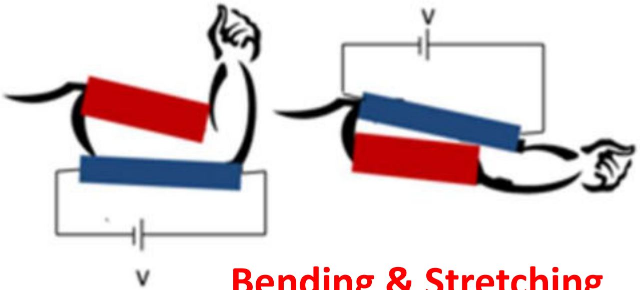
Stimulus → Response

Tactile sensor



Science Robotics 3, 22 (2018)

Artificial muscle



Bending & Stretching

Courtesy: wikipedia

Ultrahigh responsive sensors

Stretchability →

Introduction of strain dissipation mechanism into the material design itself

Molecular engineering: **soft and dynamic segments & bonds, interface compressibility**

Self-healability →

Dynamic intermolecular interaction (most effective approach)

Combination of bonds (eg. weak and strong Hydrogen bonds)

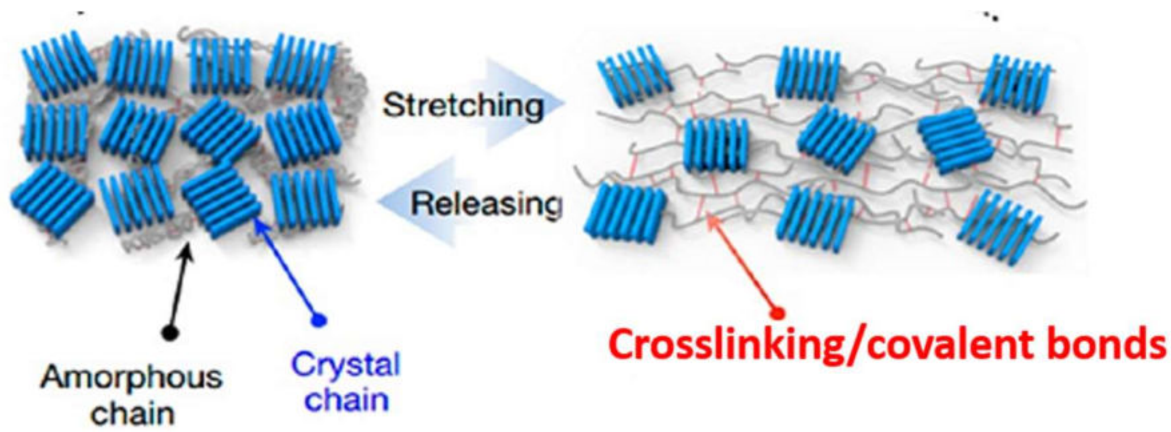
Biocompatibility →

Incorporation of biodegradable moieties along the polymer backbone

Conducting polymer composites

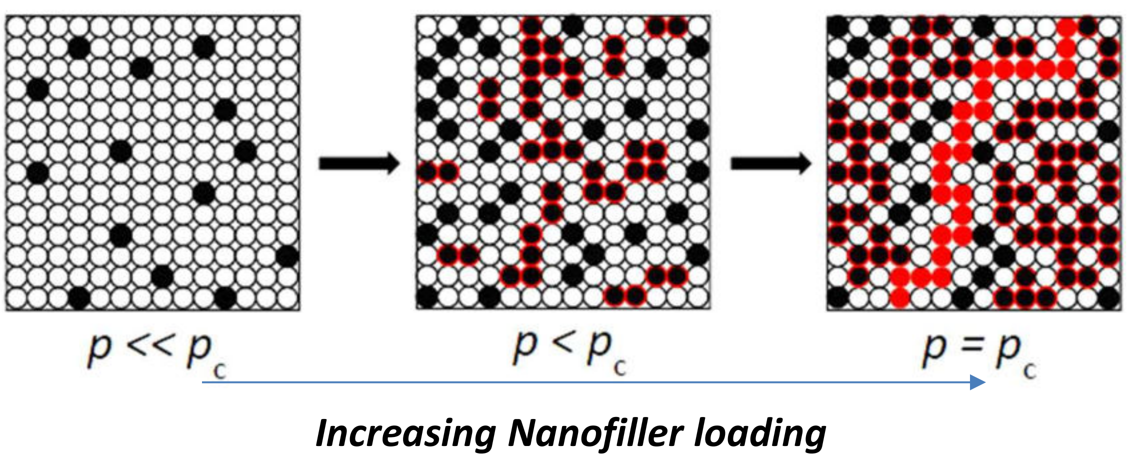
Conducting/Semi-conducting Elastomers + Nanofillers

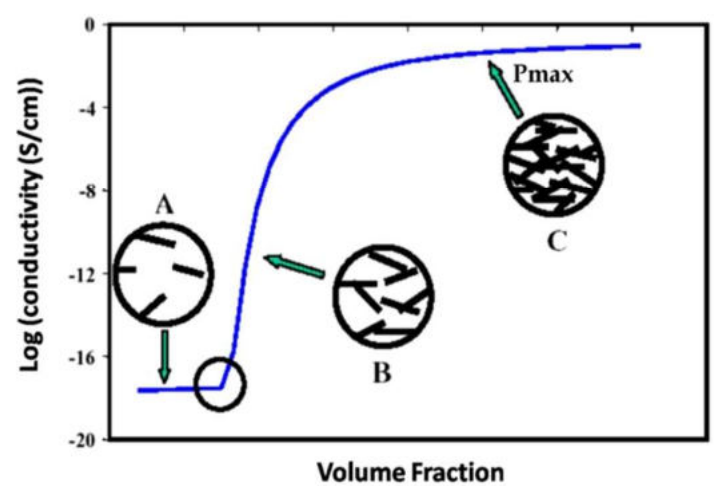
Elastomeric matrix (intrinsic stretchability)

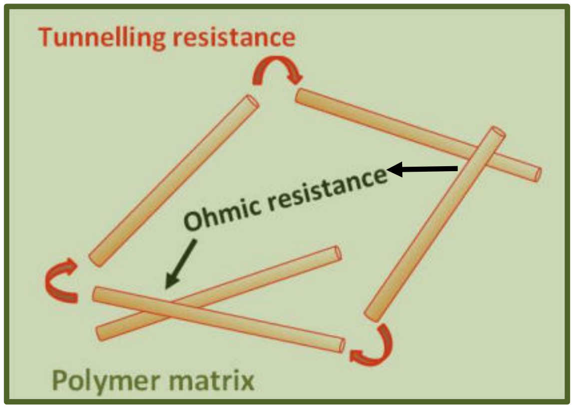


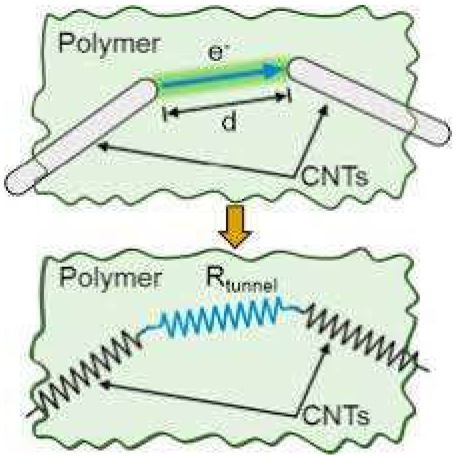
Adapted from ACS Nano 12 (2018)

Inclusion of nanofiller to matrix: Electrical response









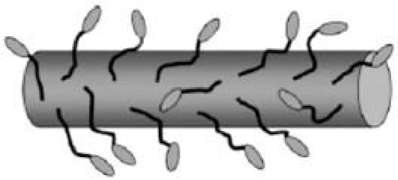
Synergy between matrix and filler : controls the functionality

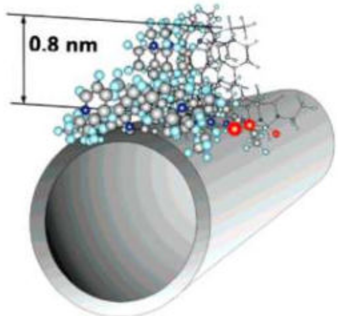
Challenge

Controlling the functionality (conduction) under external stimuli :

Constructing special phase morphology of the composite

- **Interface**
- **Interphase**
- **Matrix morphology**
- **Chain entanglements (interaction with fillers)**
- **Percolated network of nanofillers**





Radiation Processing

- Crosslinking

  Improves mechanical properties

- Degradation

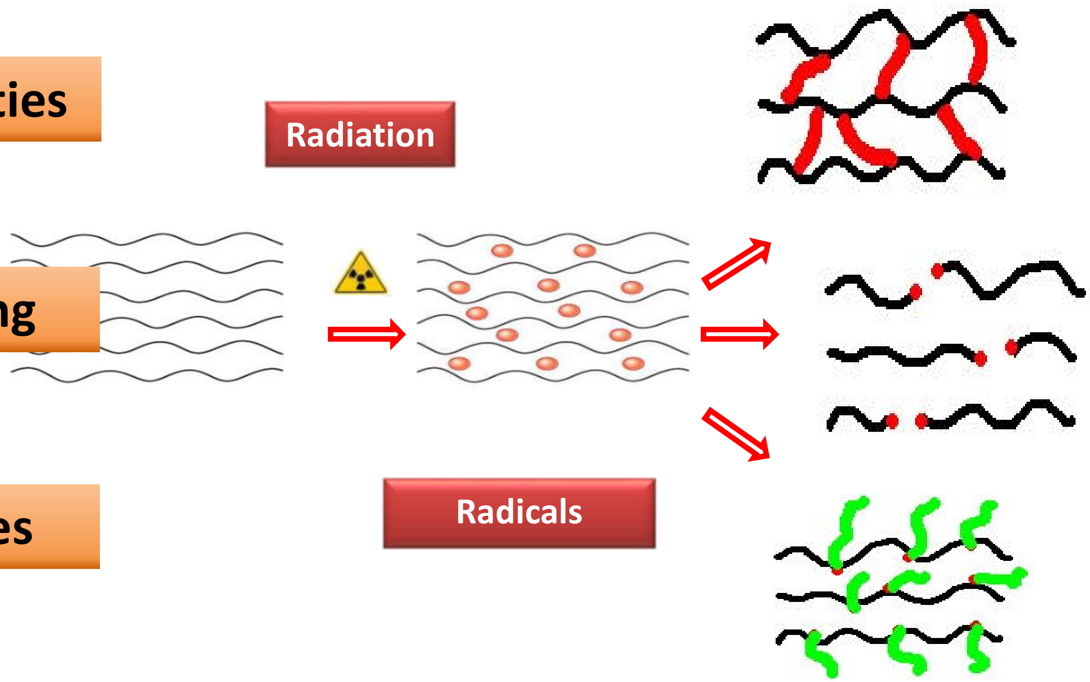
  Improves solubility/processing

- Grafting

  Adds additional functionalities

- Nanoparticle synthesis

- Oxidation



As per the application demand !

Advantage over other methods

- No need for any solvent or molecular moieties to engineer the microstructure of the base polymer matrix
- Easier and efficient way to modify the structure in an optimized manner
- Room Temperature
- High throughput

Engineering the microstructure of Polymer nanocomposite

Functional Matrix

- Elastomer/conducting polymer
- Radiation processing to improve functional characteristics

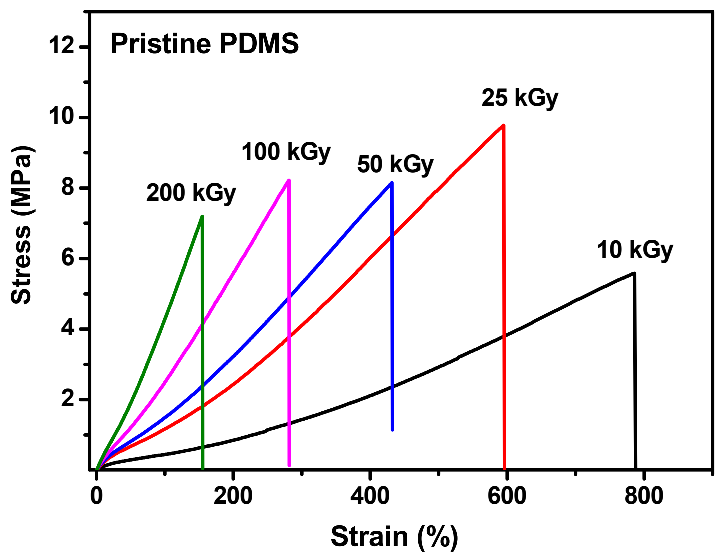
Electrical conduction

Nanofillers: CNT, nanocarbon, carbon black, Ag nanowires etc.

PDMS (Poly dimethysiloxane) and CNT/Nano carbon black (CCB)

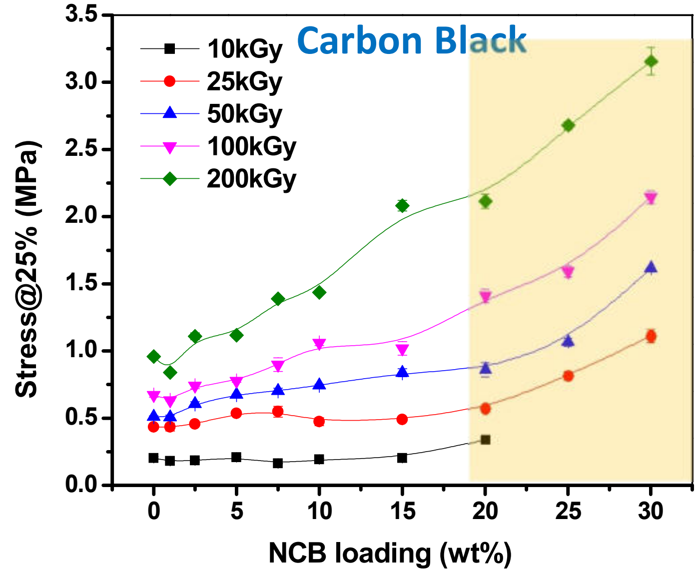
Mechanical property

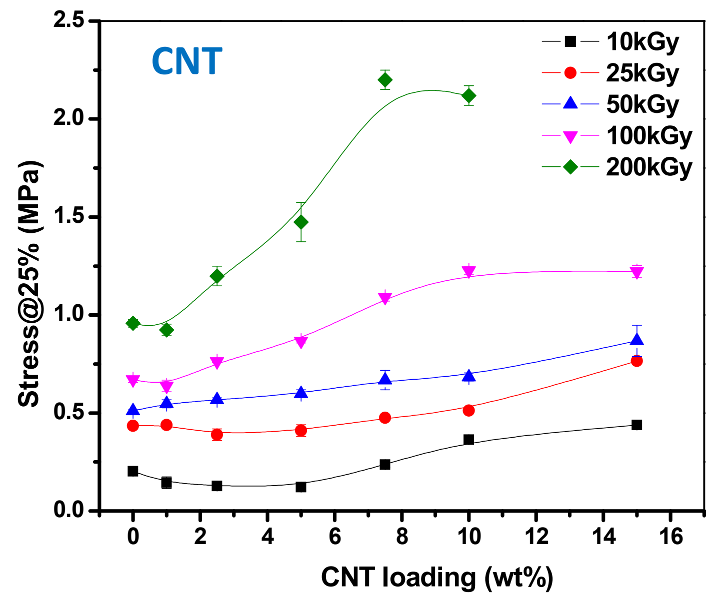
Pristine PDMS



- Crosslinking improved the mechanical response of PDMS and Nanocomposites
- Modified microstructure: Synergetic effect of crosslinking and nanofiller loading

Nanocomposites

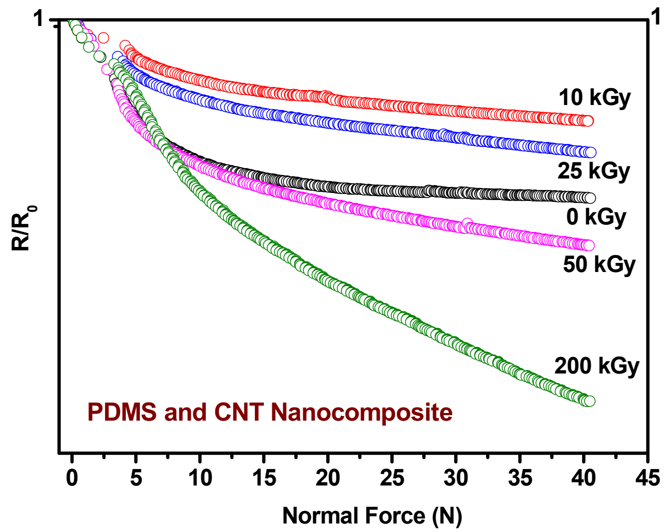


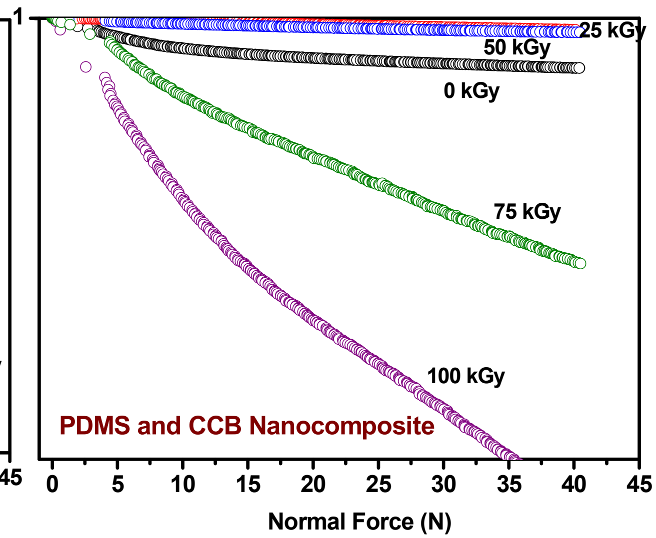


Optimization: Interplay of sensitivity vs range

Piezoresistive response

Compressive (Normal) Force



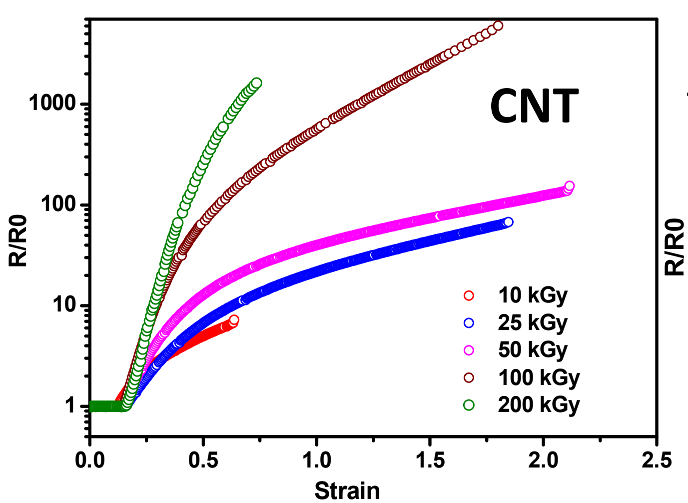


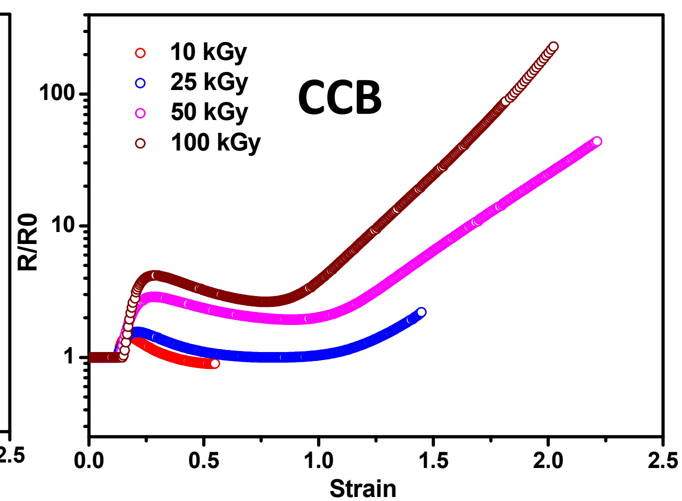
Radiation processing (crosslinking) improves the response characteristics

CNT and CCB : difference in optimum radiation dose to get the best response

Higher dose needed for CCB case (responsive @ 75 kGy)

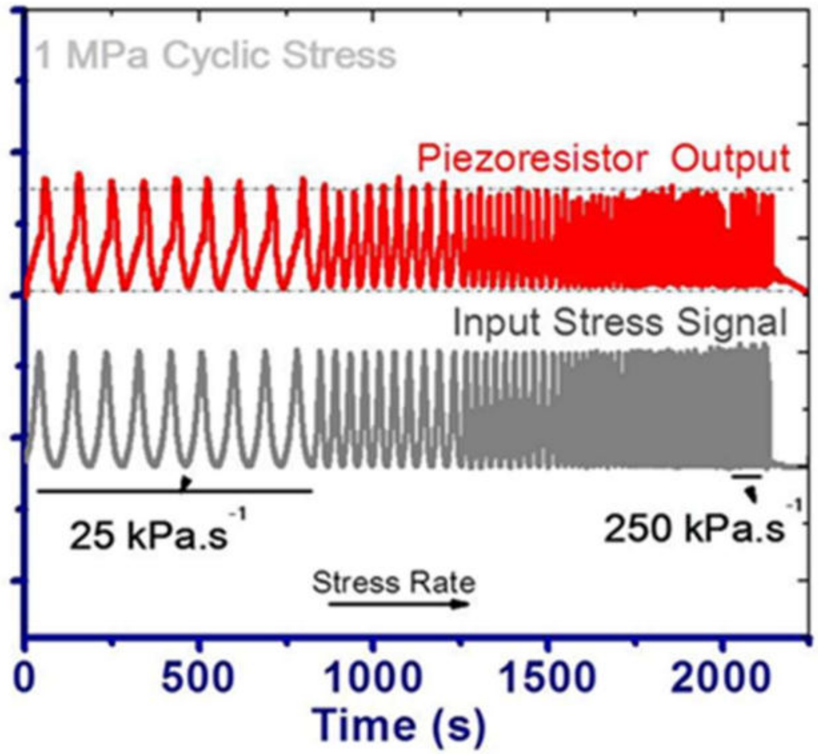
Tensile Force (stretching)

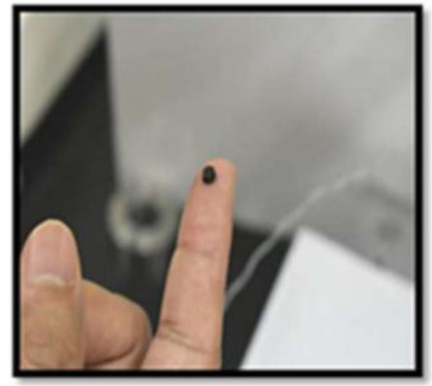




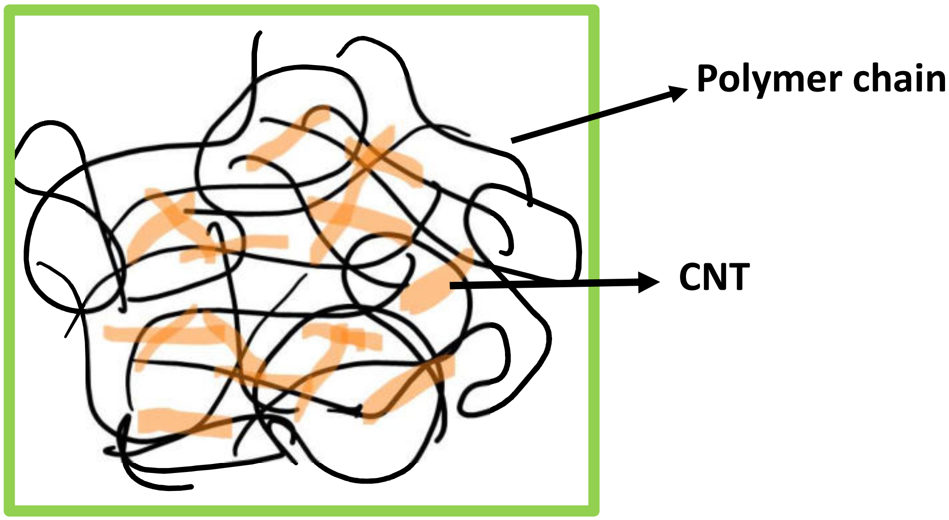
Under tensile force, CCB behaviour is different than CNT

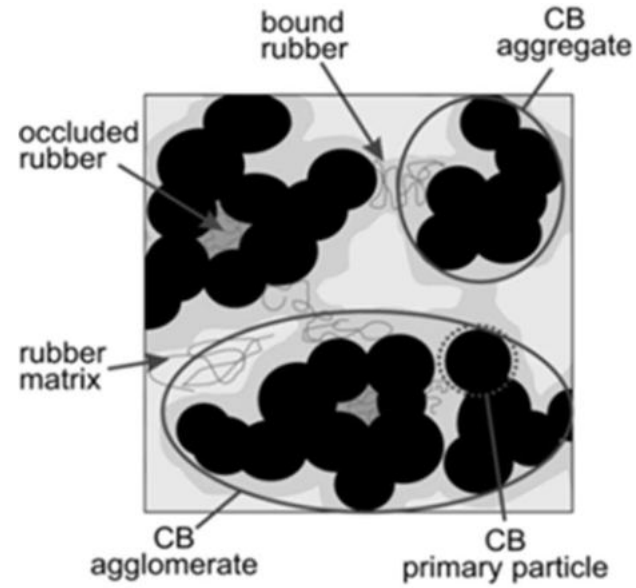
Small strains: CCB network breaks
Larger strain: role of microstructure of the matrix





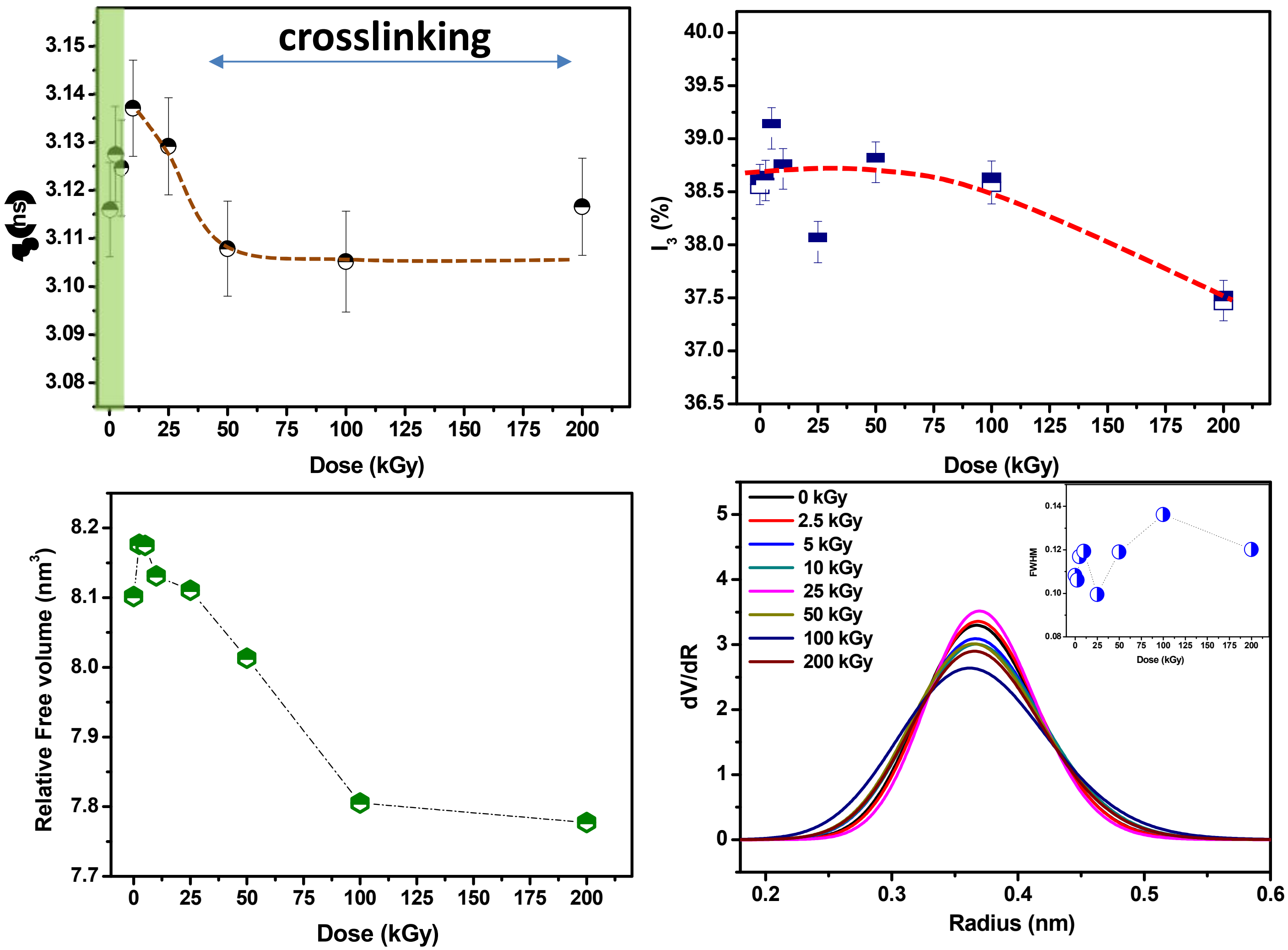
Radiation Technology based high-stress sensing piezoresistors





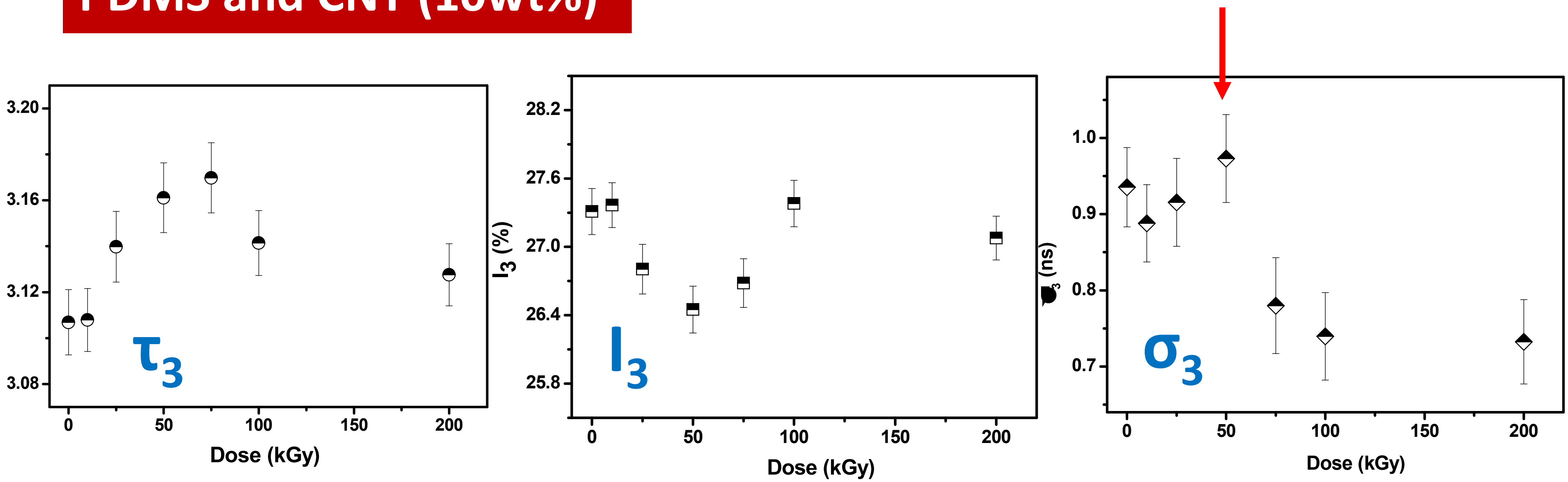
Understanding microstructural characteristics responsible for piezoresistive response

Pristine PDMS



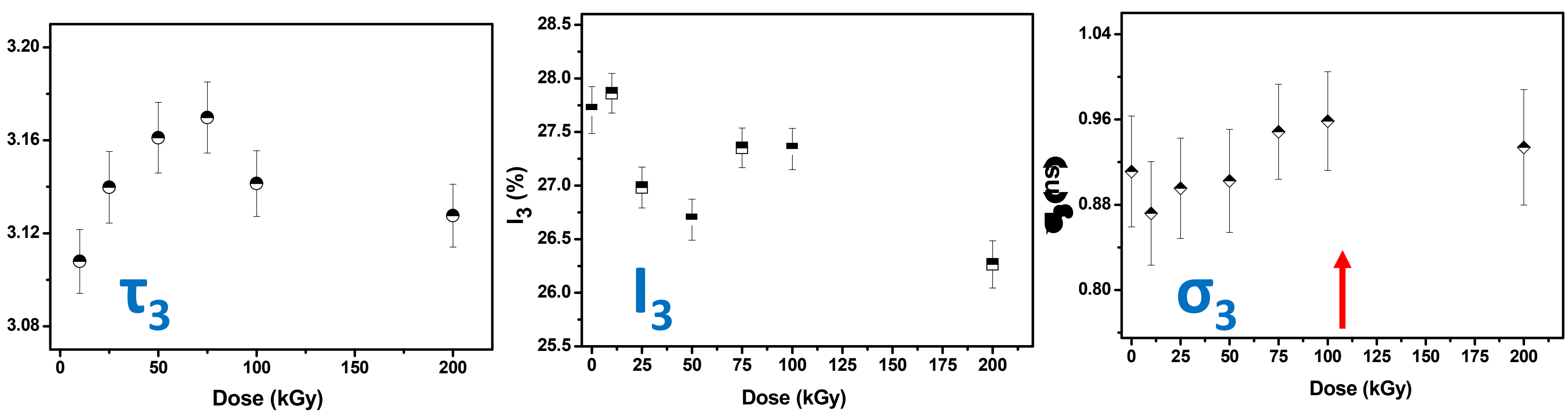
- **Decrease in free volume size with crosslinking**
- **Crosslinking: Increase in size distribution of free volumes**

PDMS and CNT (10wt%)

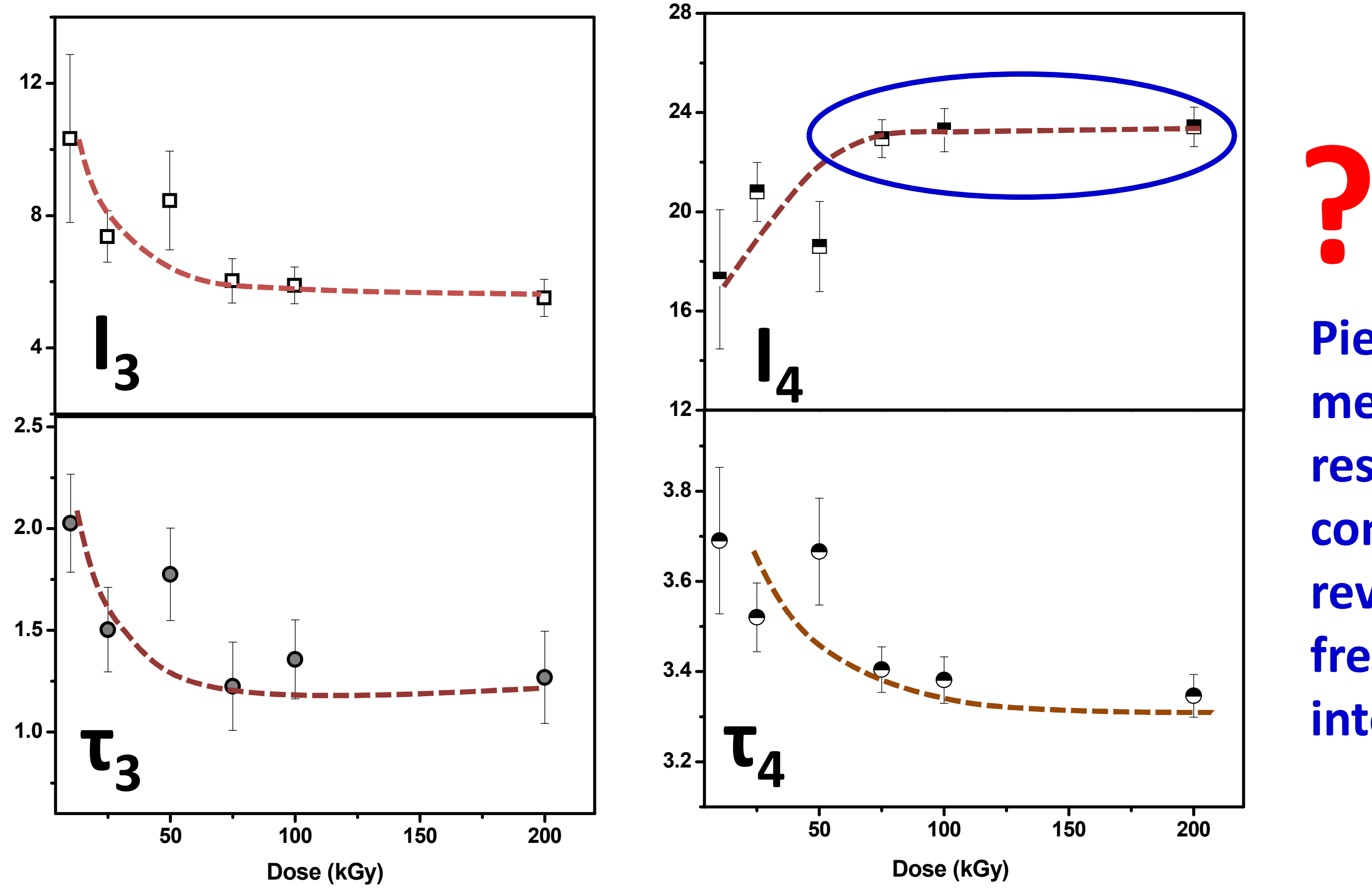


Increase in τ_3 with increase in crosslinking is counterintuitive!!

PDMS and CCB (20wt%)



PDMS and CNT nanocomposite



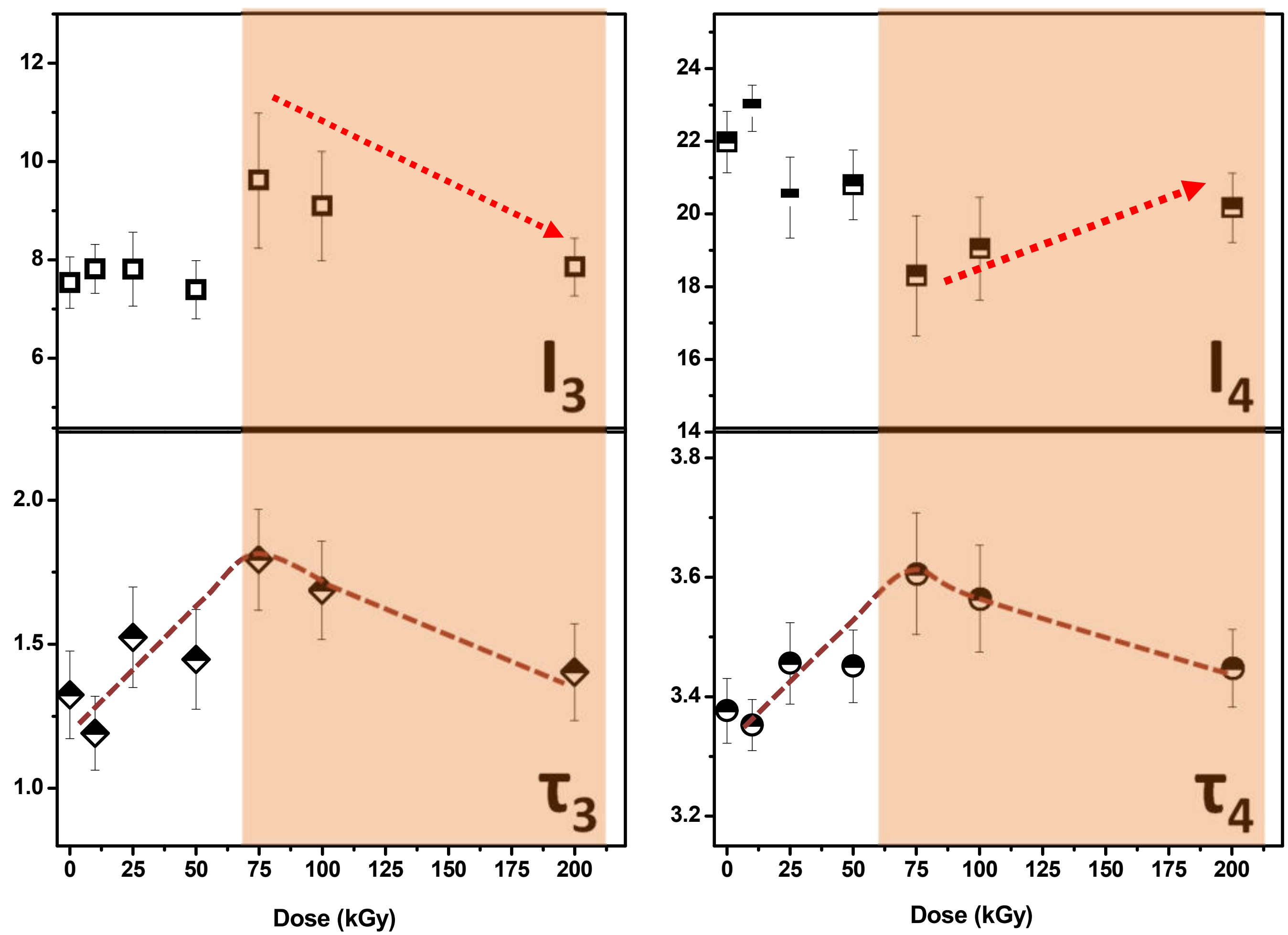
Interphase region

Bulk Polymer matrix

Piezo resistive and mechanical response of the composite do not reveal reduction of free volumes at the interphase

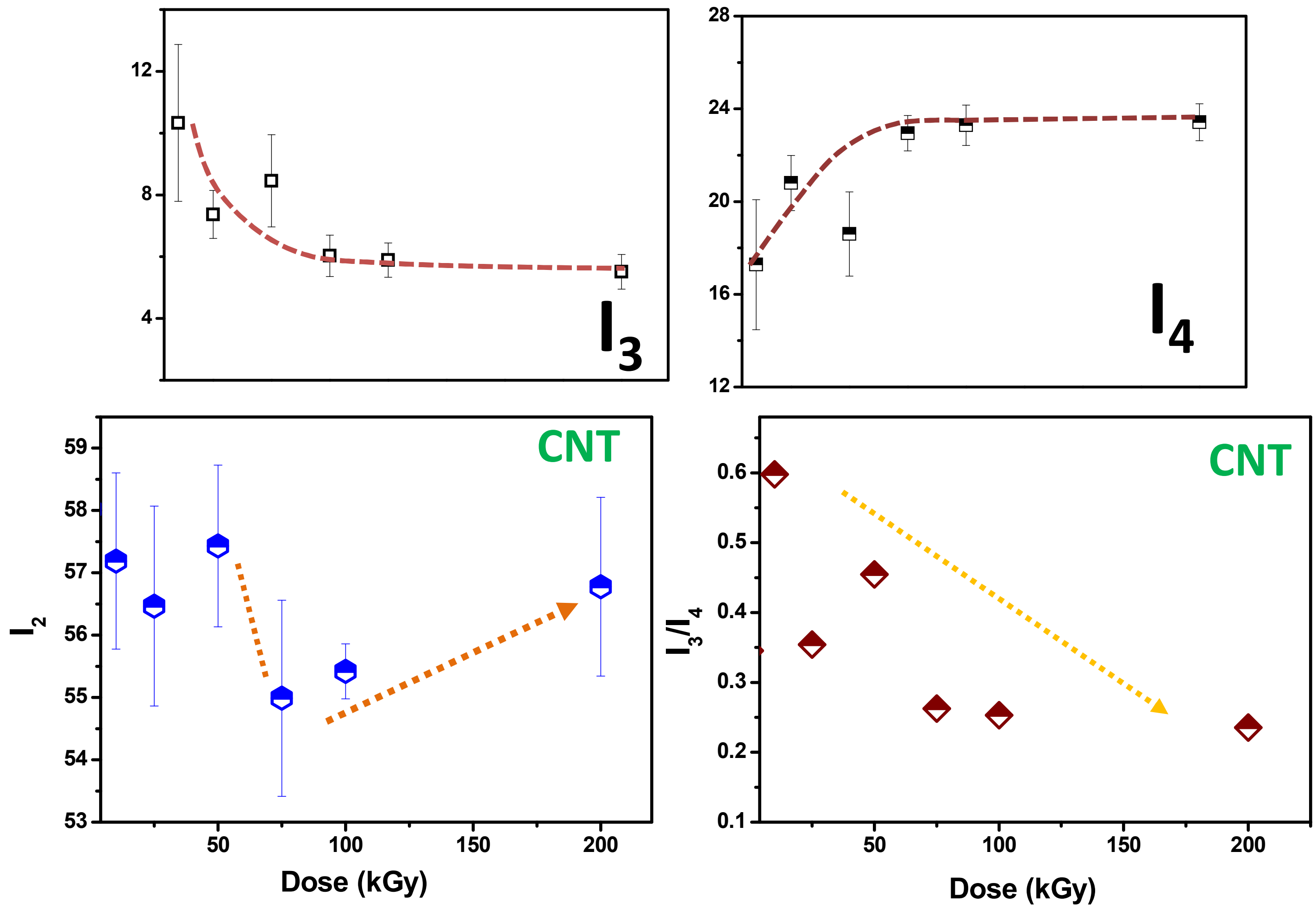
- Radiation crosslinking in both the regions (Reduction in free volume size)
- Interphase has smaller size free volumes: compact arrangement of molecules near the filler

PDMS and CCB nanocomposite



Behaviour similar to CNT above a threshold dose ~ 75kGy

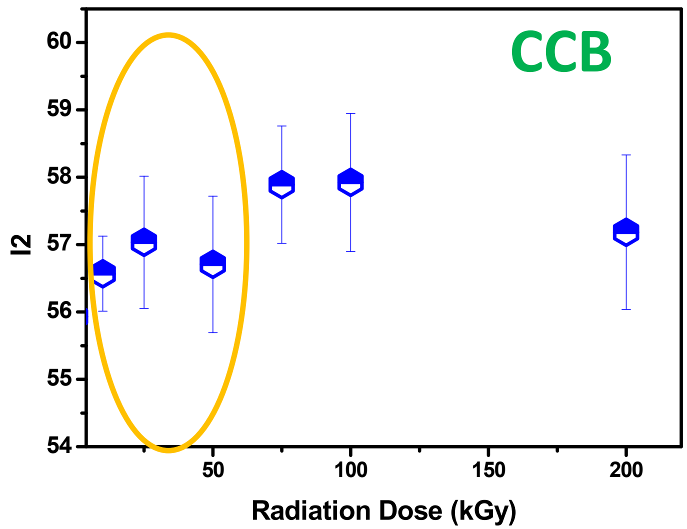
Consistent with piezoresistive response

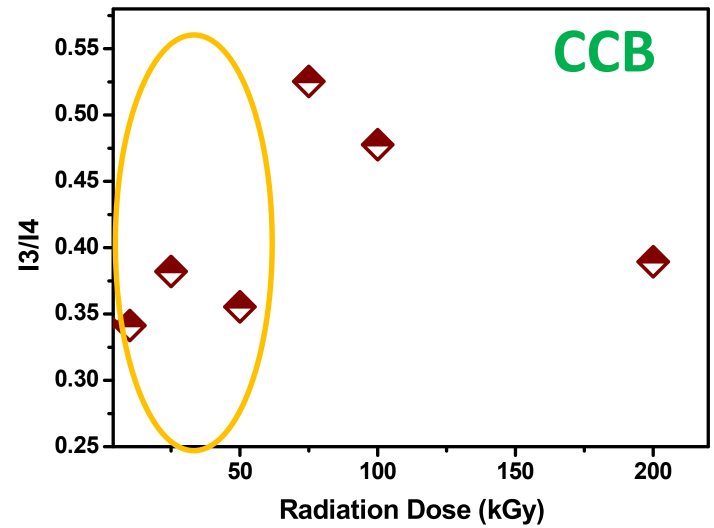


Change in I_3 and I_4 : Two possibilities

Ps formation probability in the interphase region: Spur model

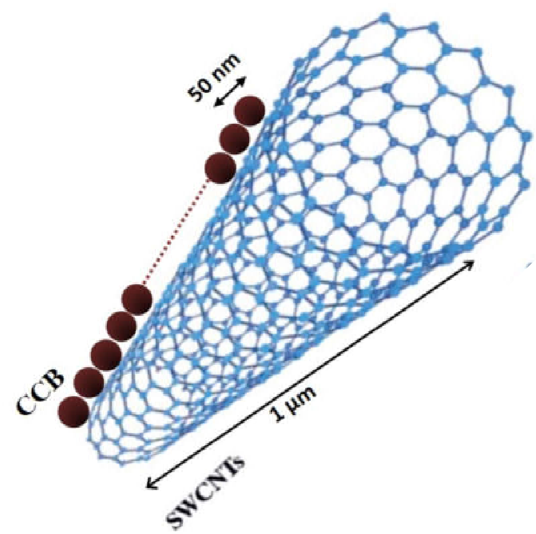
Ps migration from smaller free volumes to larger ones

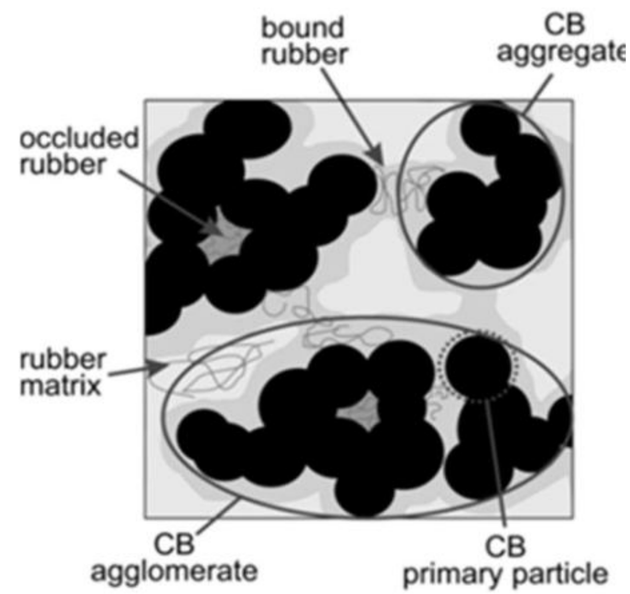




Difference in the interaction of CCB and CNT with Polymer matrix ?

Microstructure at lower doses in CCB?

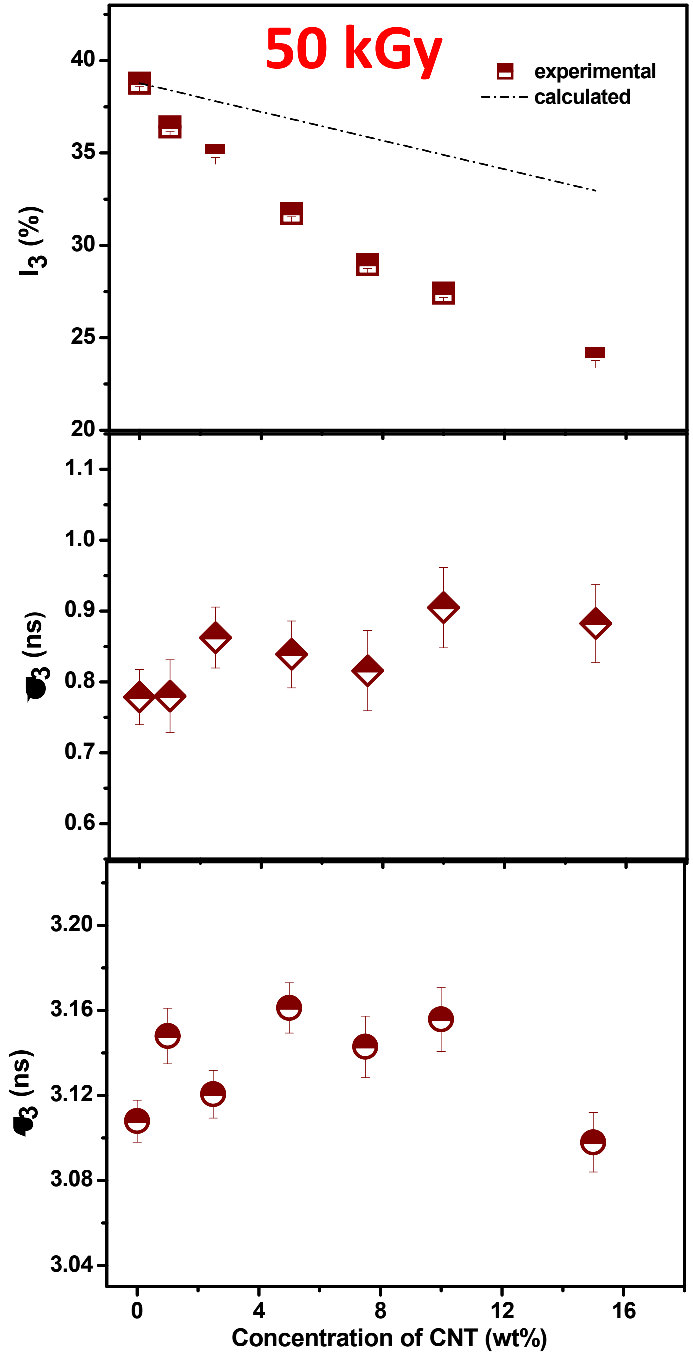




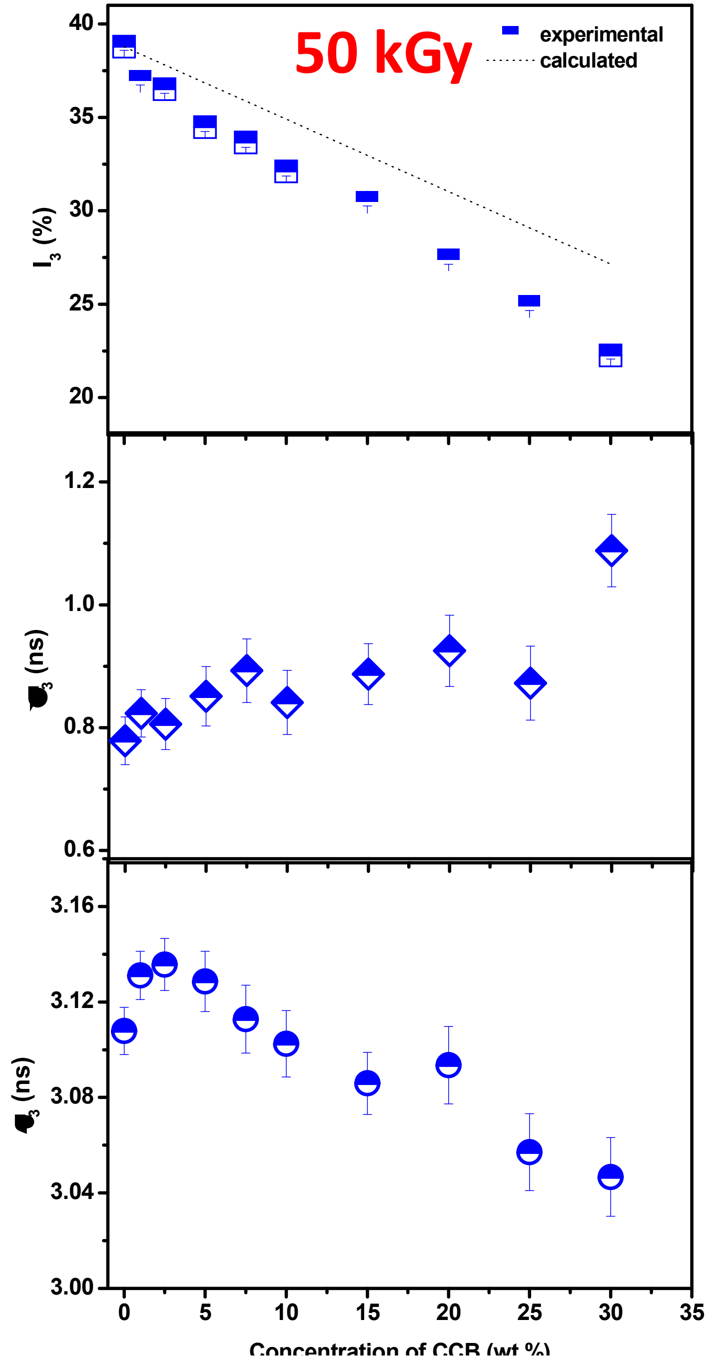
Nanocomposites with varying loading of nanofillers

- **Microstructure alteration**
- **Enhanced conductivity**

CNT



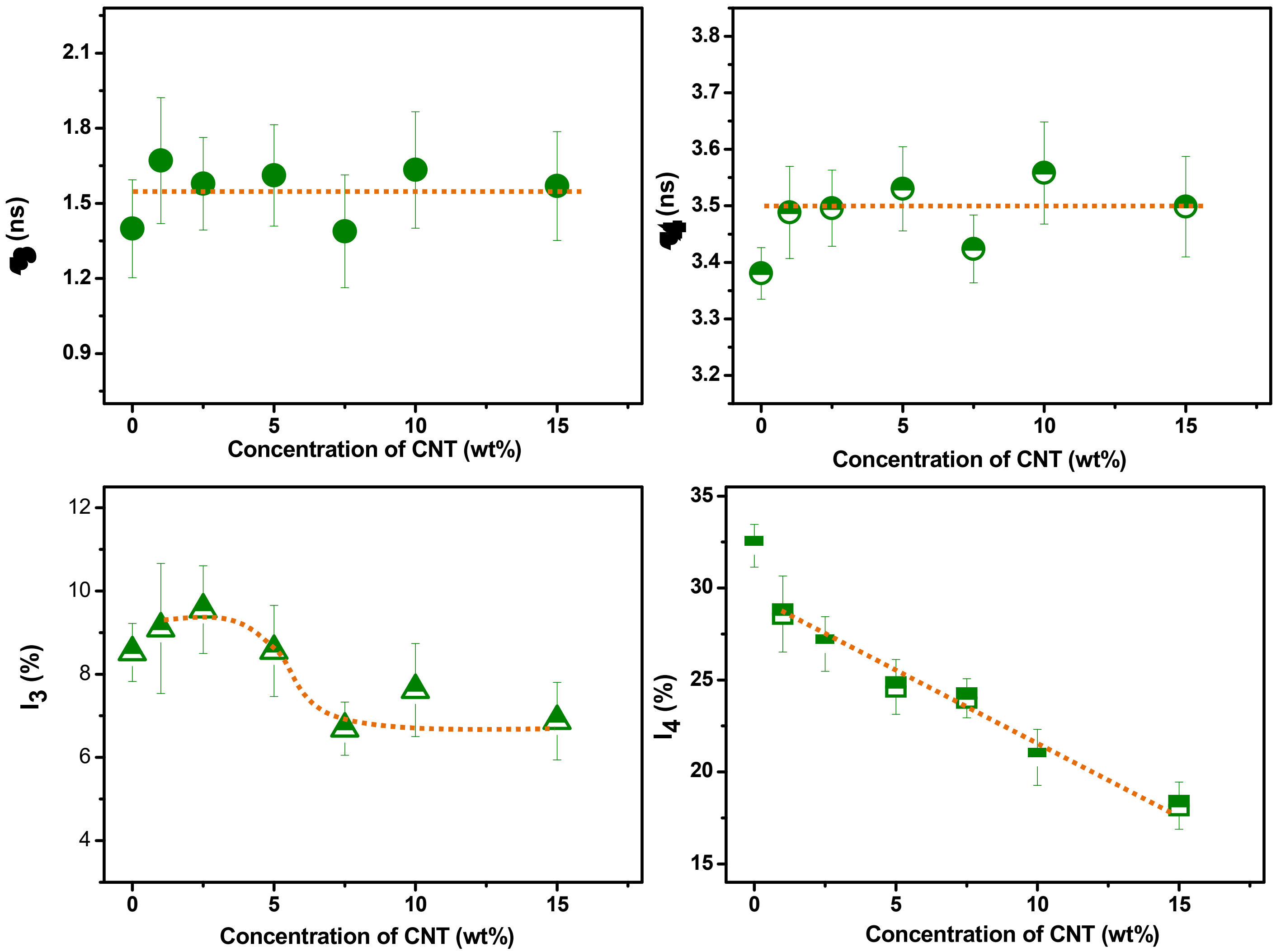
CCB



Interacting system of carbon nanofiller and PDMS

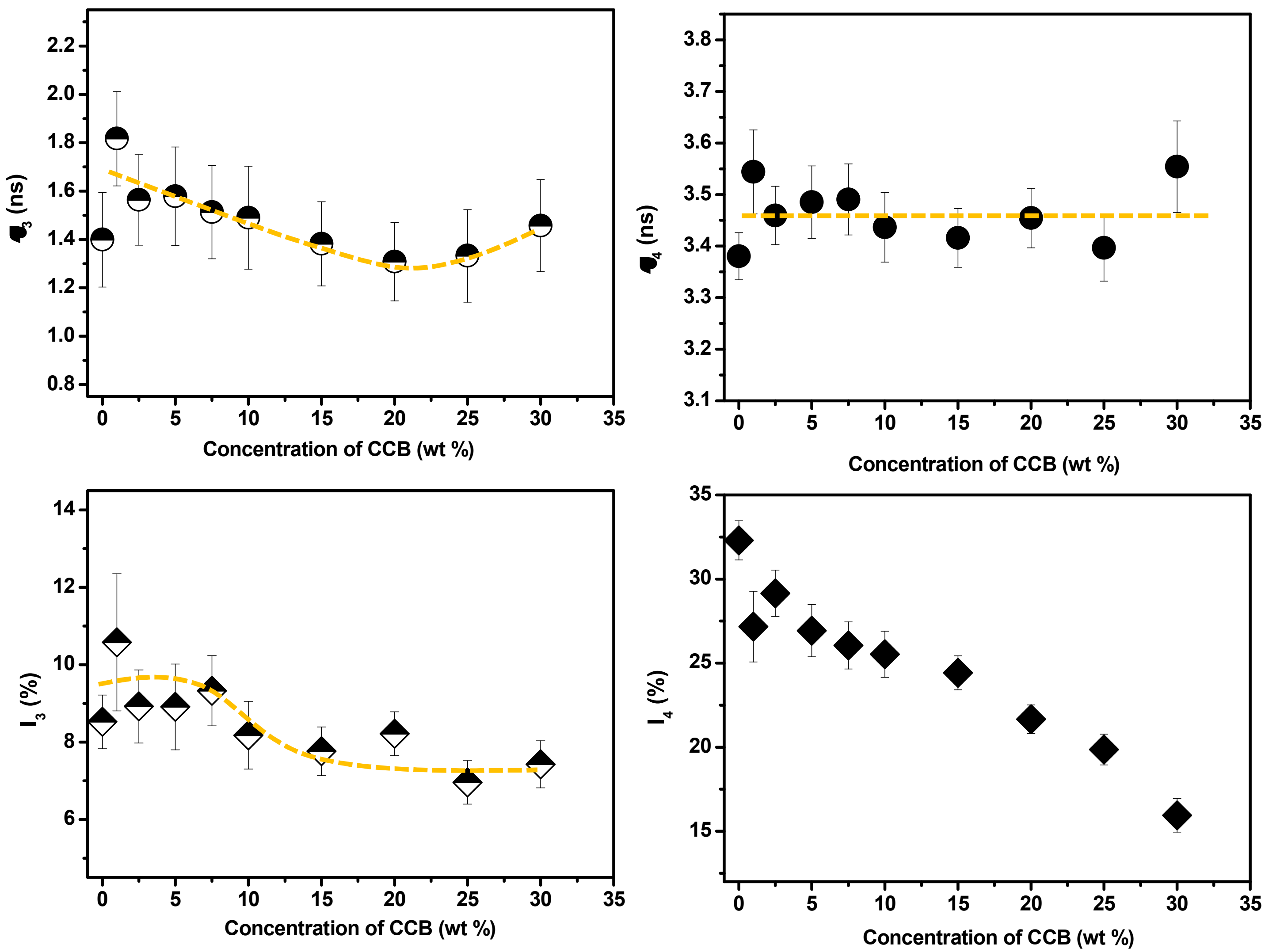
Microstructure of CNT and CCB based composite is different

CNT @ 50 kGy



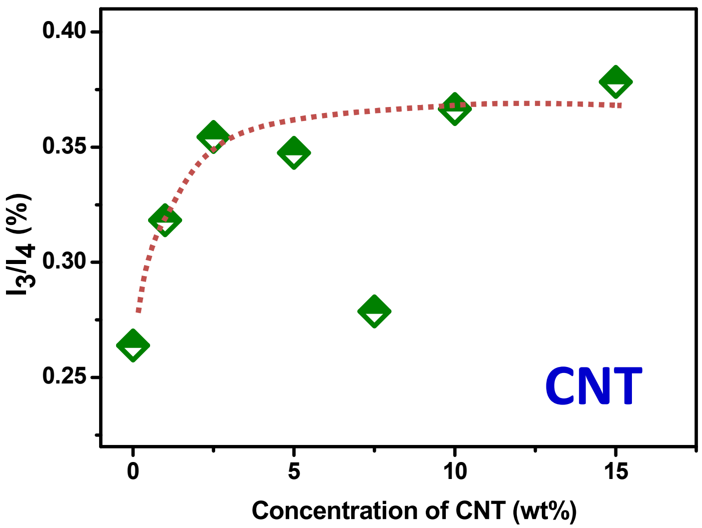
No appreciable change in free volume characteristics of interphase and bulk polymer region

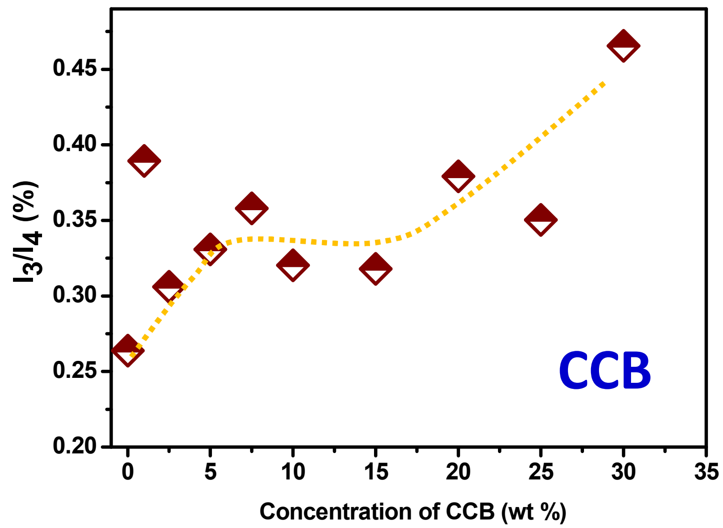
CCB @ 50 kGy



τ_3 (ns)
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0 5 10 15 20 25 30 35
Concentration of CCB (wt %)
τ_4 (ns)
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
0 5 10 15 20 25 30 35
Concentration of CCB (wt %)
I_3 (%)
14
12
10
8
6
0 5 10 15 20 25 30 35
Concentration of CCB (wt %)
I_4 (%)
35
30
25
20
15
0 5 10 15 20 25 30 35
Concentration of CCB (wt %)

Relative fraction/concentration of free volumes at interphase





Fraction of interphase region relative to total free volume increases with increase in the nanofiller loading but behaviour is different in CNT and CCB

I_3 and I_4 profiles certainly an indicative of microstructural characteristics

Summary

- Microstructure of the base polymer matrix is one of the crucial factors for the response of sensors
- Microstructure engineering using radiation and nanofiller ingression is a route to optimize the response
- Positron probing of free volume is a sensitive way to decipher microstructural alterations in nanocomposites
- The influence of varying electron density (conducting nanofiller) on positron annihilation parameters (Ps formation probability etc…) needs to be systematically investigated in order to elucidate microstructure characteristics and its correlation with the response .

Acknowledgement

- Dr. P. K. Pujari
- Dr. Abhinav Dubey and Dr. R. K. Mondol
- Colleagues from Nuclear Probe section