

## **POLYIMIDE CELLULOSE NANOCRYSTAL COMPOSITE AEROGELS**

### **Abstract**

Polyimide (PI) aerogels are highly porous solids having low density, high porosity and low thermal conductivity with good mechanical properties. They are ideal for various applications including use in antenna and insulation such as inflatable decelerators used in entry, decent and landing operations. Recently, attention has been focused on stimuli responsive materials such as cellulose nano crystals (CNCs). CNCs are environmentally friendly, bio-renewable, commonly found in plants and the dermis of sea tunicates, and potentially low cost. This study is to examine the effects of CNC on the polyimide aerogels. The CNC used in this project are extracted from mantle of a sea creature called tunicates. A series of polyimide cellulose nanocrystal composite aerogels has been fabricated having 0-13 wt of CNC. Results will be discussed.



# Polyimide Cellulose Nanocrystal Composite Aerogels

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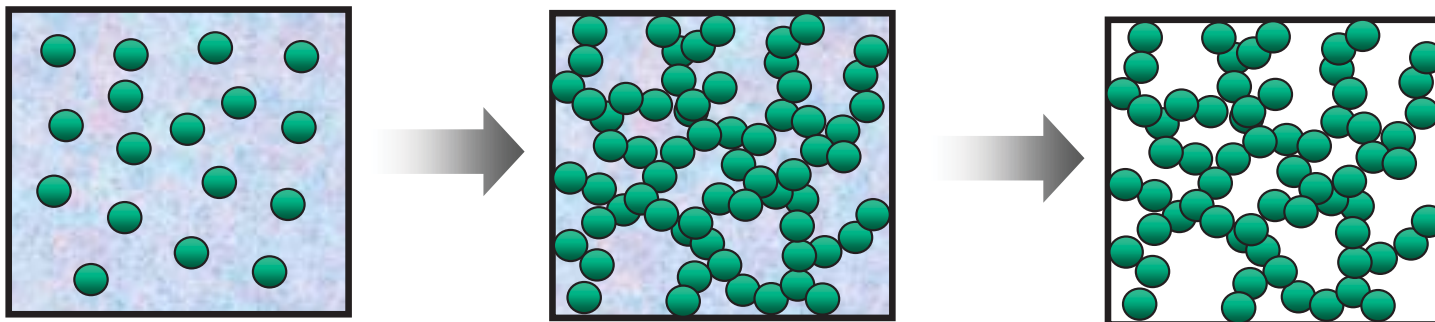
Stuart J. Rowan, CWRU

Elvis Cudjoe, CWRU

Anna Sandberg, Summer Intern



# What are aerogels?



Sol

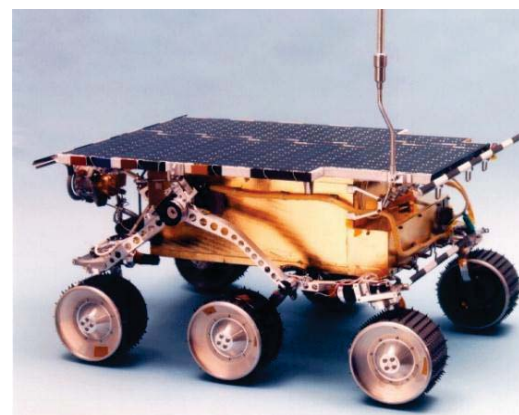
Gel

Aerogel

- Highly porous solids made by removing liquid portion of a wet gel
- Nanometer scale pore size (10 – 40 nm)
- High porosity (> 90%) and surface area (200 – 650 m<sup>2</sup>/g)
- Low density (< 0.3 g/cm<sup>3</sup>)

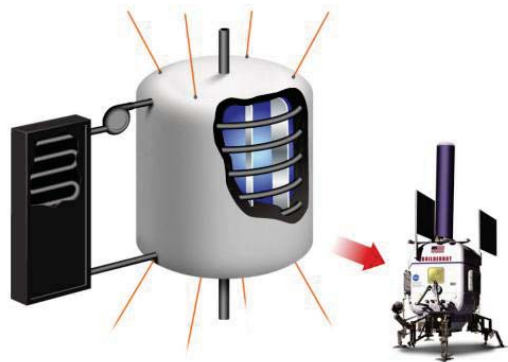


Cosmic dust collector  
Stardust Mission



Rover battery insulation

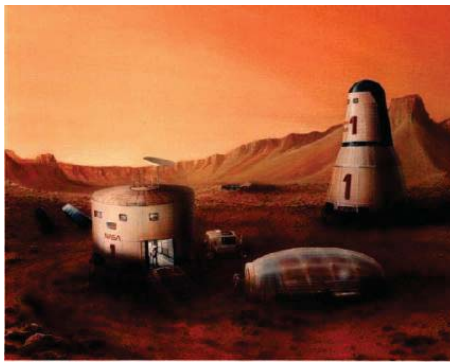
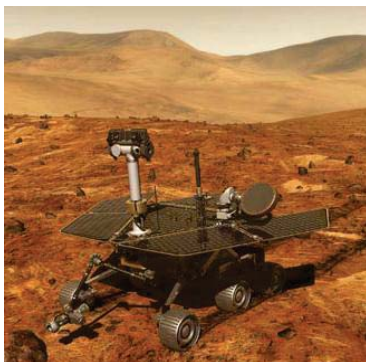
# Possible applications



Cryotank Insulation



Insulation for EVA suits, habitats and rovers



Ultra-lightweight, multifunctional structures for habitats, rovers



Inflatable Decelerator

# Aromatic polyimide aerogels

- Low thermal conductivity
- High temperature stability (short term)
- Moisture resistance depending on backbone chemistry
- Improved mechanical properties
- Flexible and durable
- Easy to manufacture into thin film



## Objective:

- Crosslinked polyimide aerogels
- Incorporation of a nano filler to further enhance physical and mechanical properties - cellulose nanocrystals (CNCs)





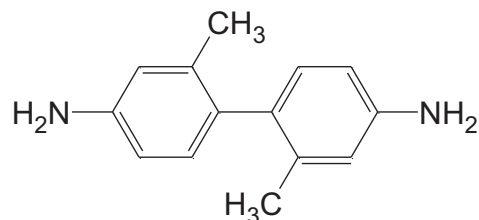
# Cellulose nanocrystals (CNCs)

- Bio-renewable, potentially low cost
- Exist in most plants and can be found in dermis of some mammals
- Can easily be modified with different charge densities or functionalities
  - make them compatible with different solvents and polymers
- Possibility to gain further mechanical strength and/or stimuli responsive behaviors
  - Flexible in water, rigid in air, etc
- CNC extracted from the mantles of a sea creature called a tunicate (tw-CNC) with aspect ratio of 80:1

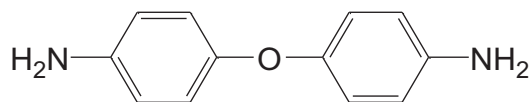


# Monomers used

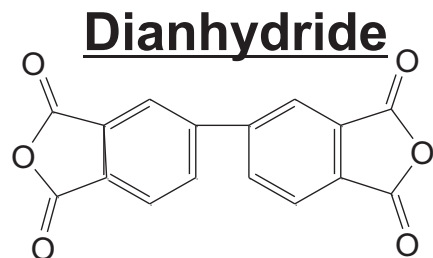
## Diamines



2,2'-Dimethylbenzidine  
(DMBZ)

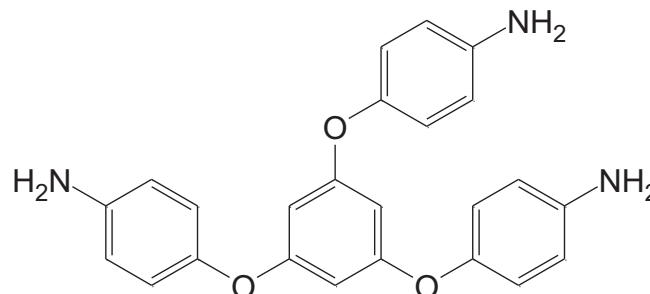


4,4'-Oxydianiline  
(ODA)



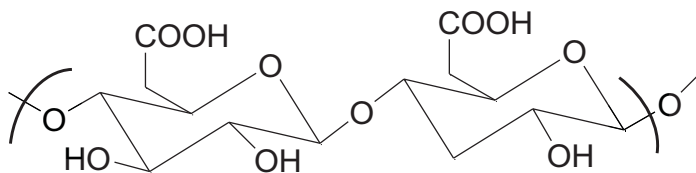
3,3',4,4'-Diphenyl  
tetracarboxylic dianhydride  
(BPDA)

## Triamine



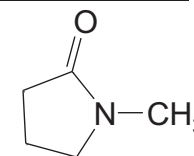
1,3,5-Triaminophenoxy benzene  
(TAB)

## Nano filler



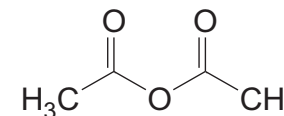
Acid functional cellulose nanocrystals  
(tw-CNC)

## Solvent



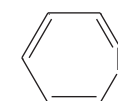
N-methyl-2-pyrrolidinone  
(NMP)

## Water Scavenger



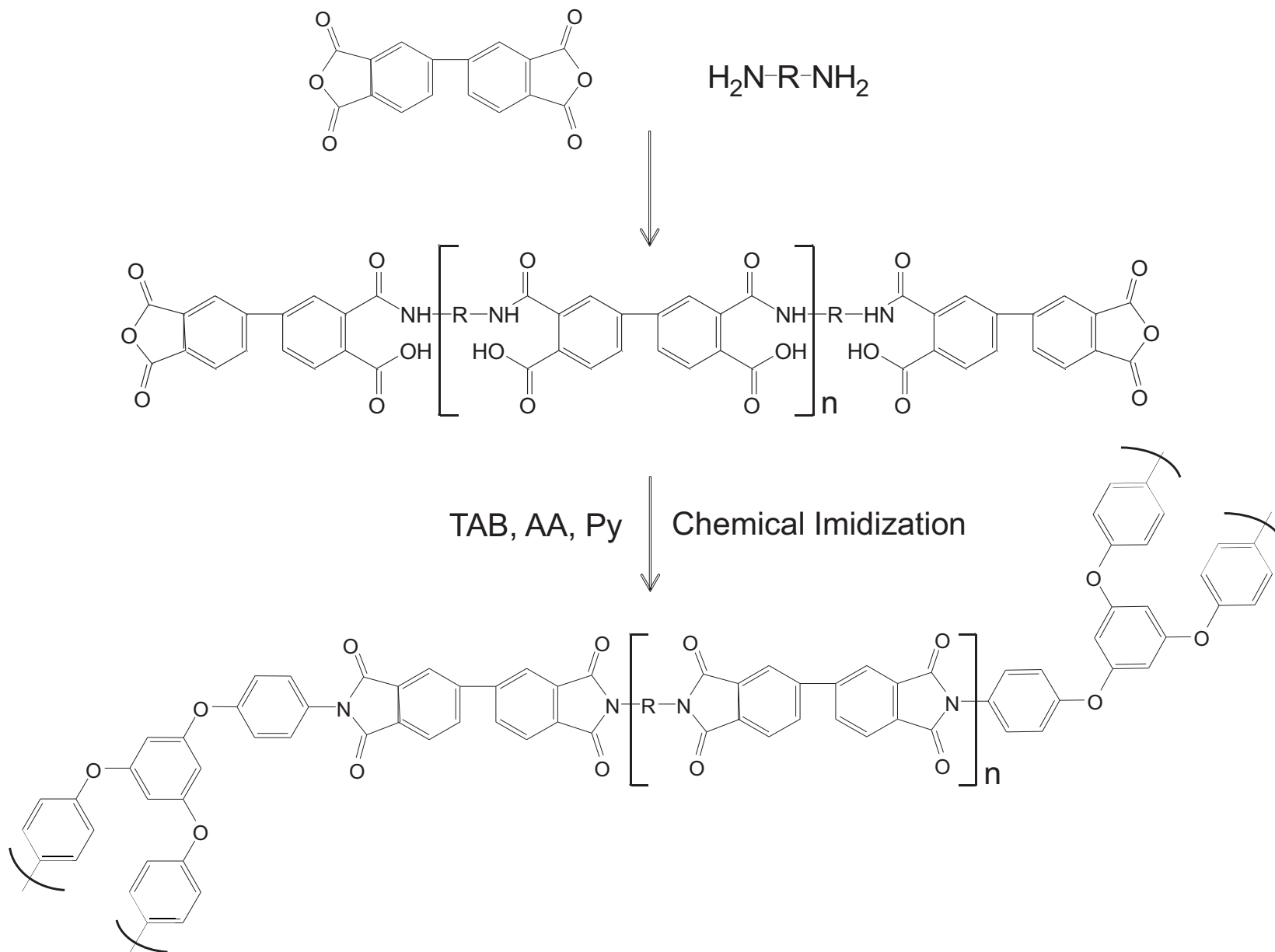
Acetic anhydride  
(AA)

## Catalyst



Pyridine  
(Py)

# Chemical imidization at room temperature







# Compositions

## Concentration of total solids in solution:

- Solid concentration =  $(\text{g total solid})/(\text{g solution}) = 7.5 \text{ wt}\%$
- Total solid weight = g polymer + g CNC
- Repeat units,  $n = 30$

## Diamine variation on the backbone:

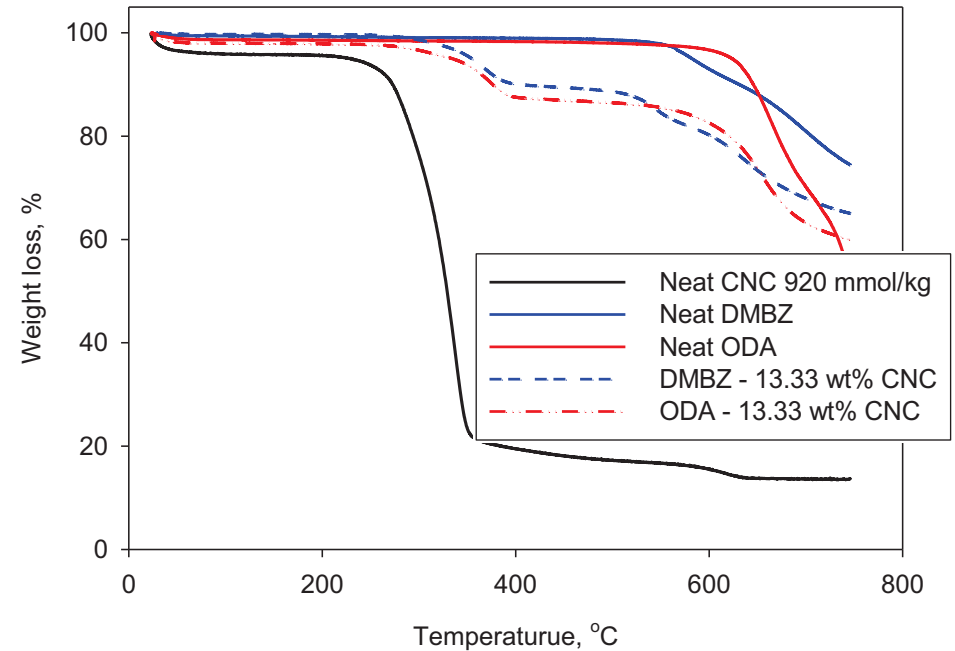
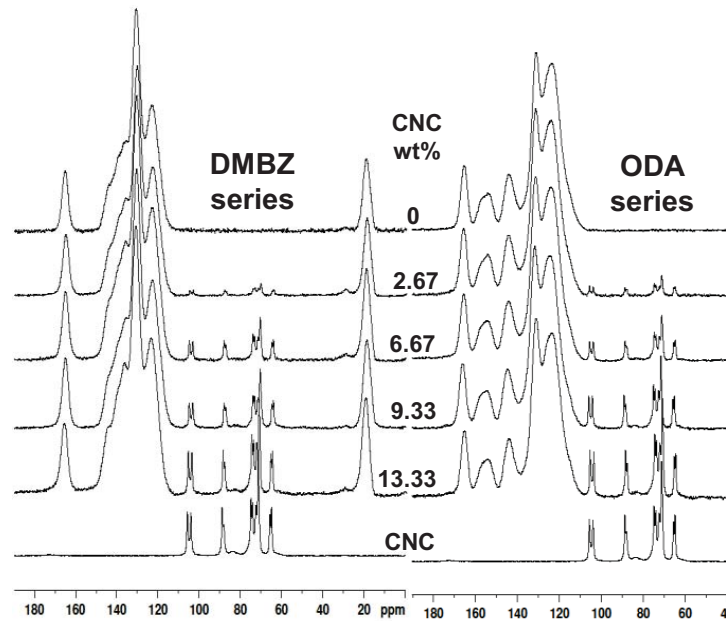
- 100 mol% DMBZ
- 100 mol% ODA

## CNC loading:

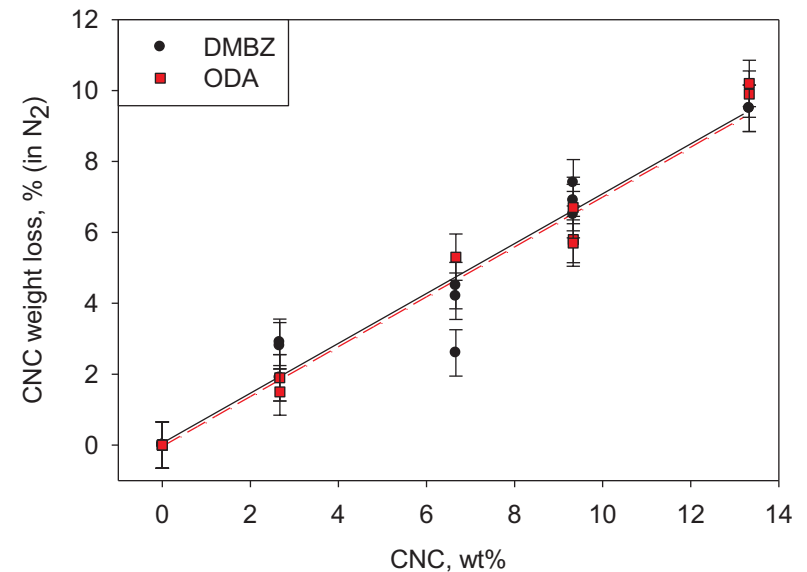
- 0 – 13.33 wt% of total solid
- CNC concentration =  $(\text{g CNC})/(\text{g CNC} + \text{g polyimide})$



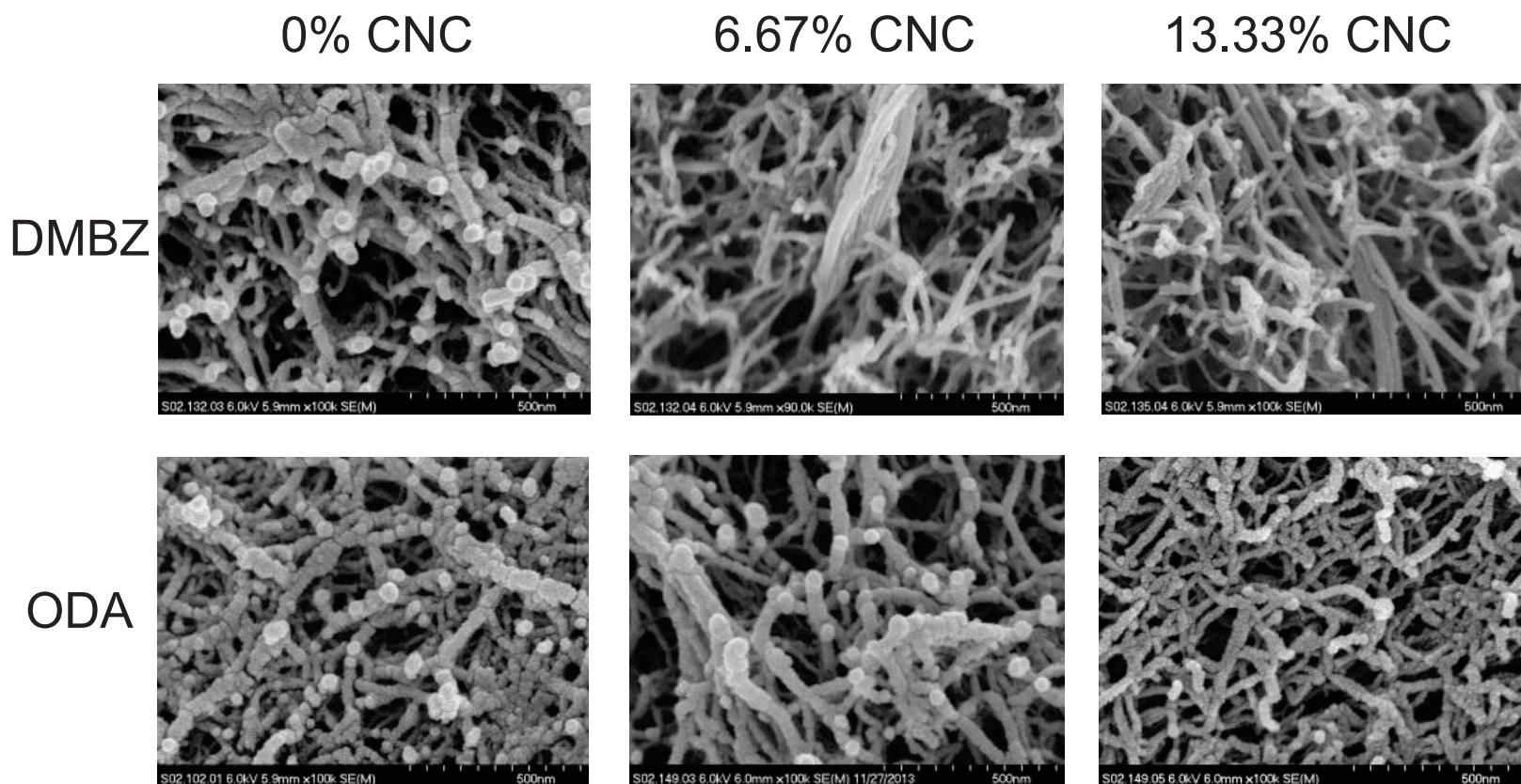
# NMRs and TGAs: Evidence of CNC in the matrix



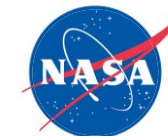
- CNC can be detected using NMR
- Can be quantified by TGA
- Same wt. loss in both sets of aerogels
- Low calculated CNC wt loss than formulated → interaction between CNC and PIs
- Higher  $T_d$ s of CNC → effect of aromatic PIs
- Lower  $T_d$ s of PIs → effect of aliphatic CNC



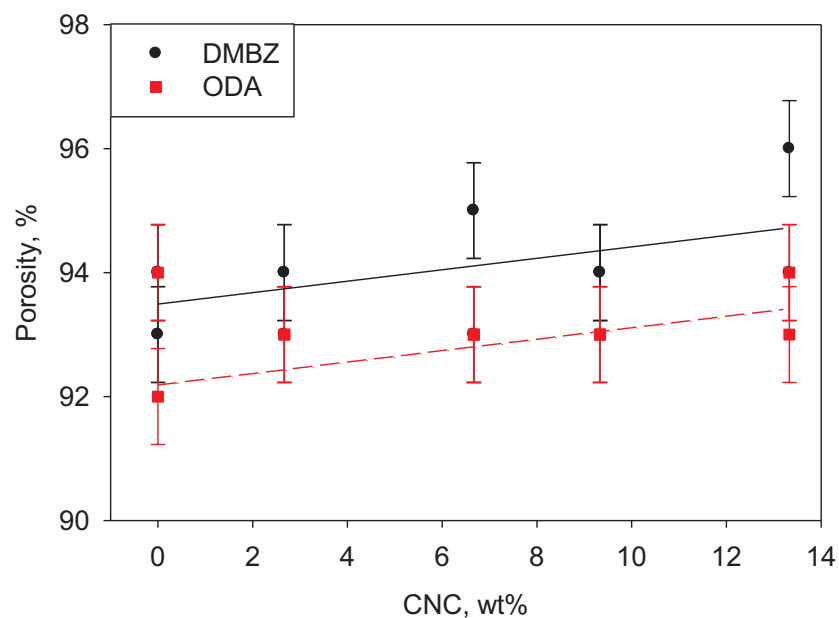
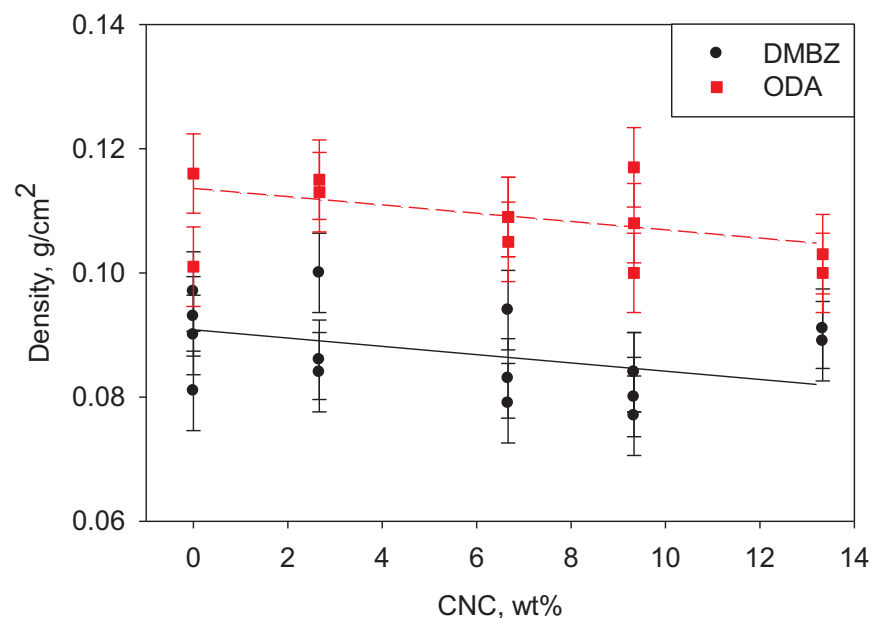
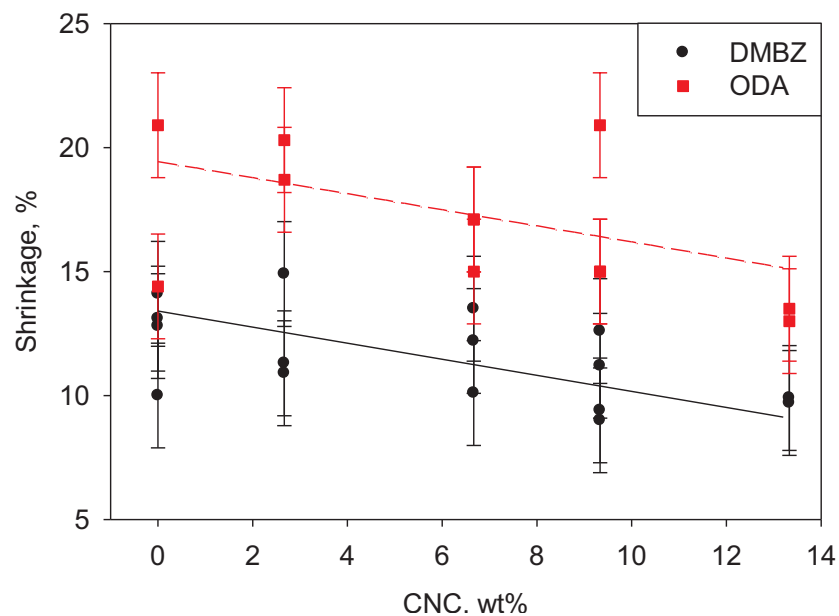
# Scanning Electron Micrographs (SEMs): No difference in pore structure



Aerogels with DMBZ in the backbone are more porous



# Incorporation of CNC improves physical properties

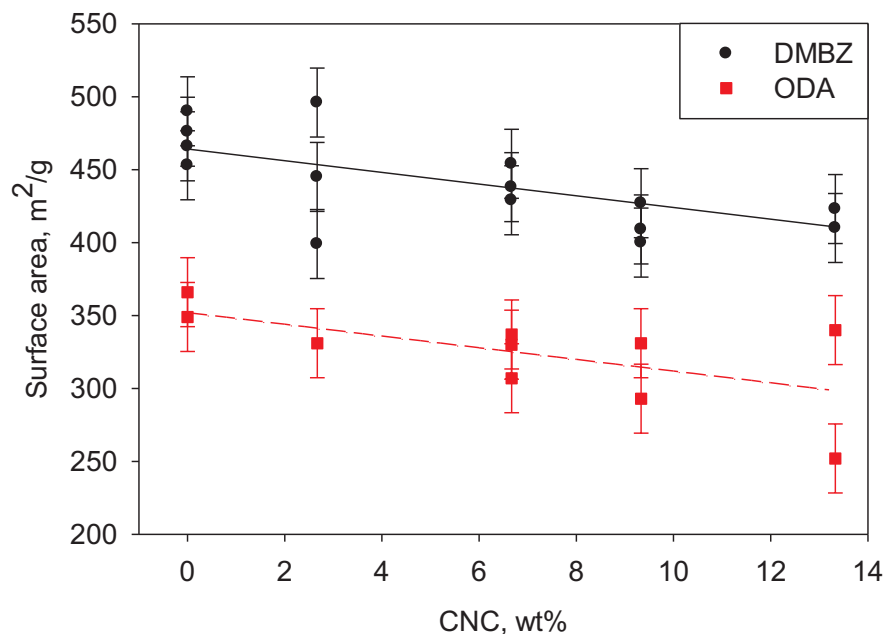


At higher CNC loading and more rigid backbone:

- Lower %shrinkage
- Lower density
- Higher % porosity



# Brunauer-Emmet-Teller (BET) surface area

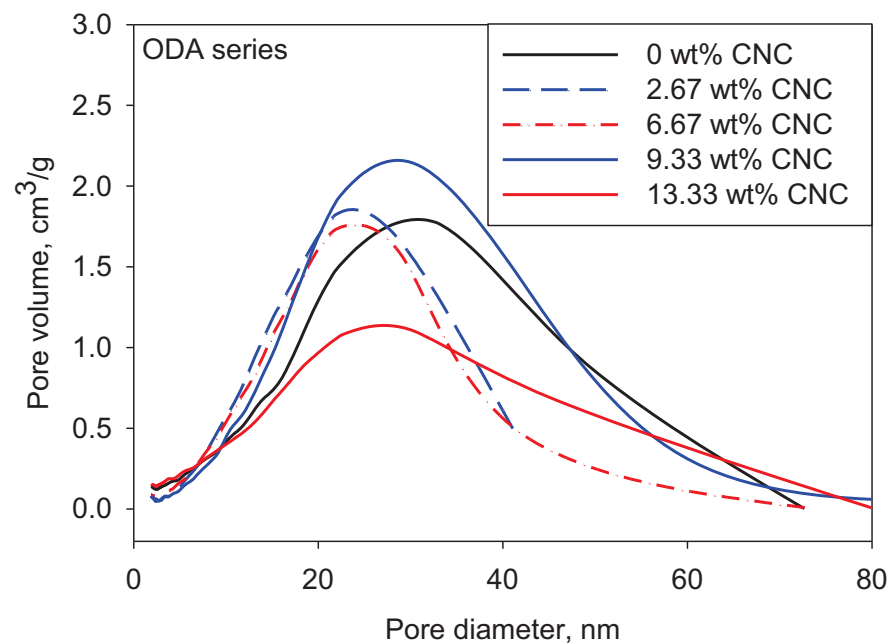
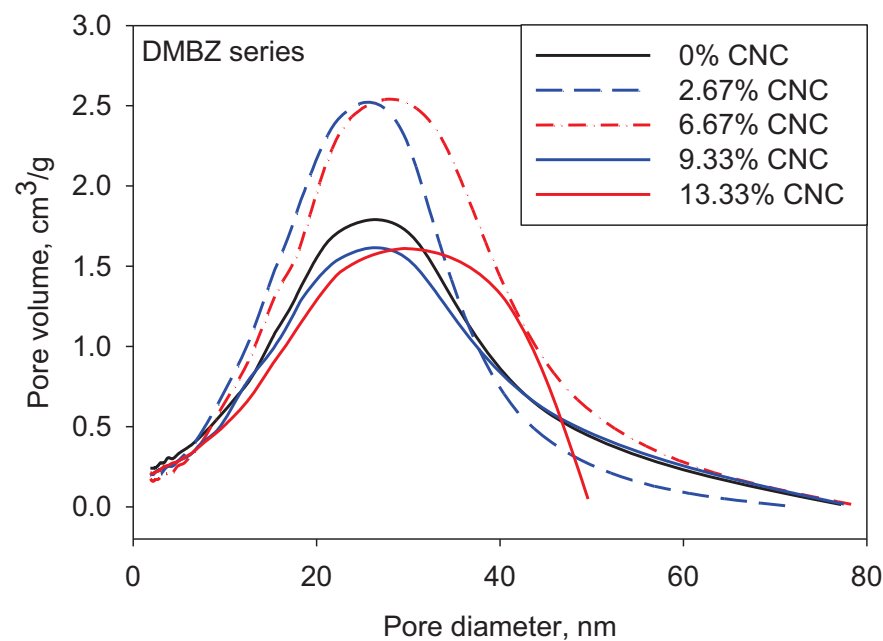


## At higher CNC loading:

- Lower BET surface area
- Larger pore diameter
- Wider pore diameter distribution

## DMBZ vs. ODA:

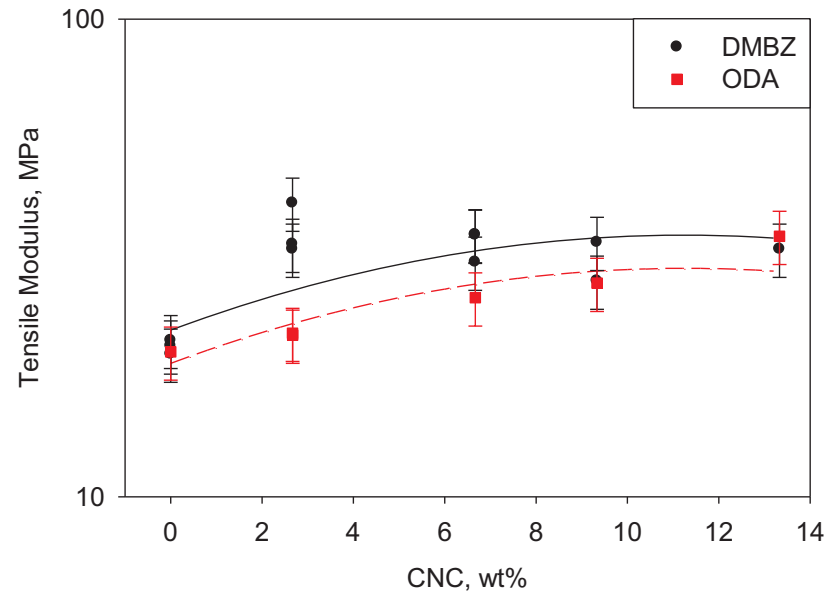
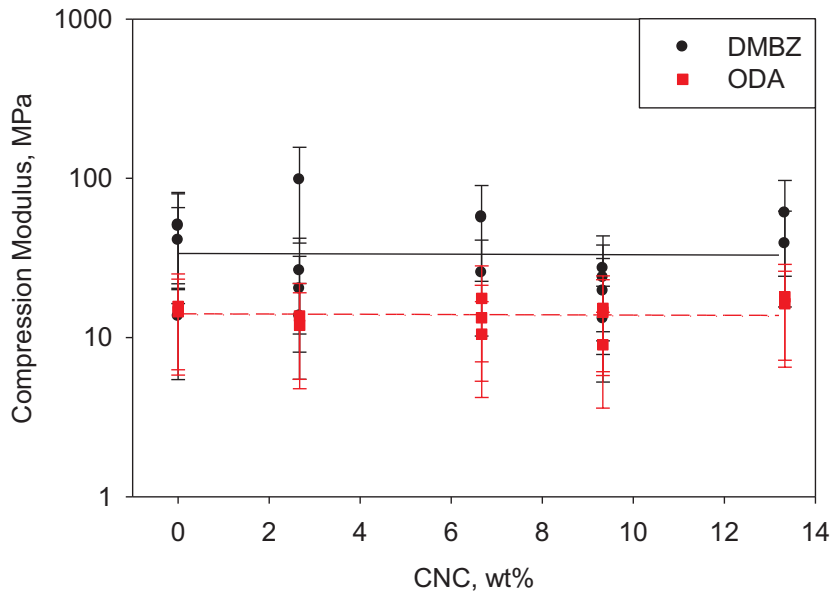
- Higher pore volume
- Narrower pore diameter distribution







# Improves mechanical properties at high CNC loading

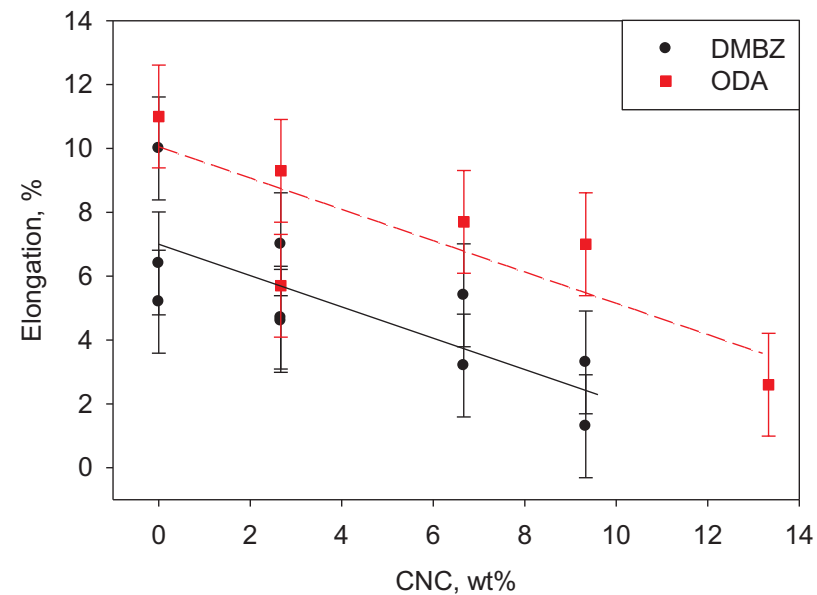


## Higher CNC loading:

- Slight decrease in compression modulus (density dependent)
- Higher tensile modulus
- Lower % elongation

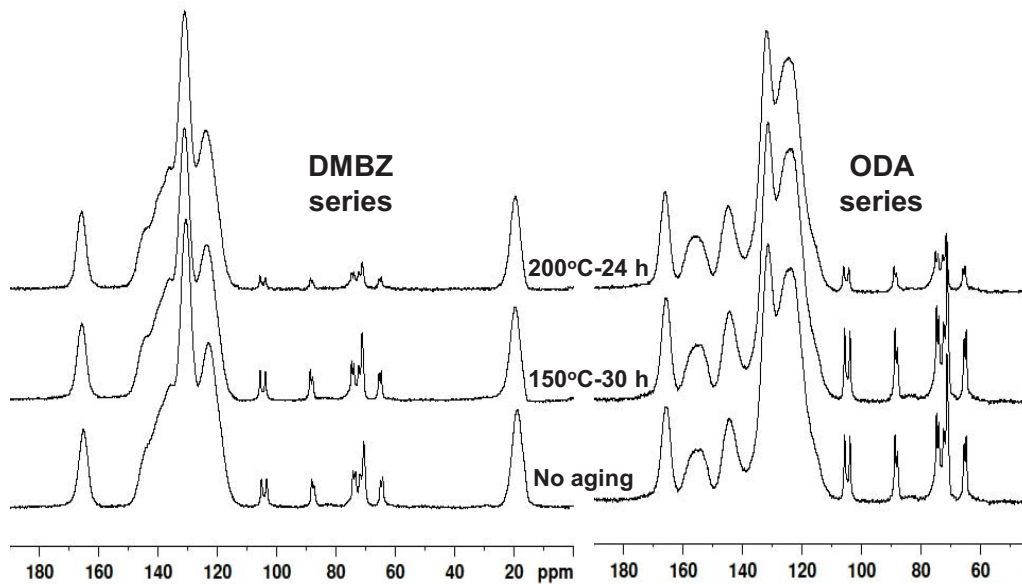
## More rigid backbone:

- Higher modulus (density independent)
- Lower % elongation

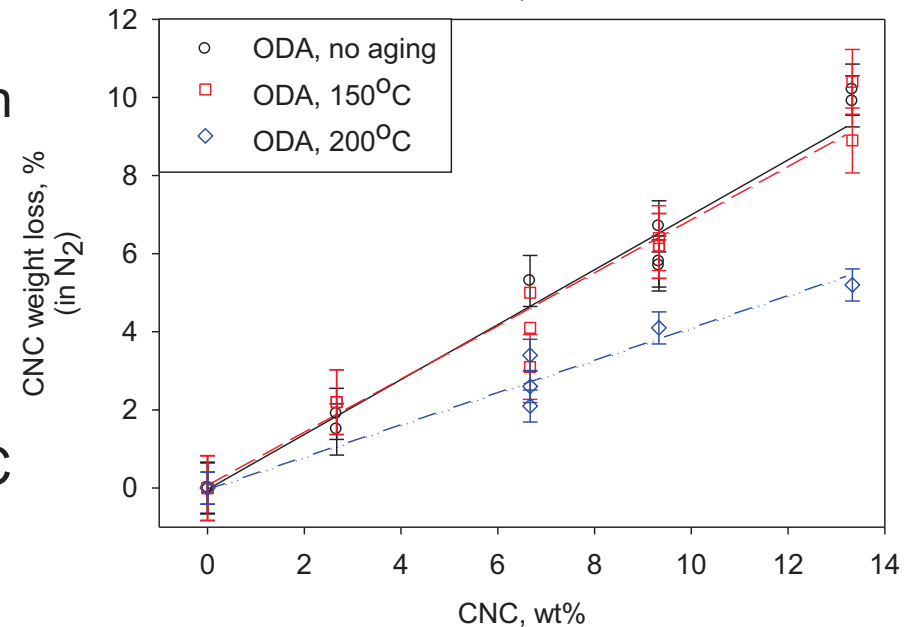
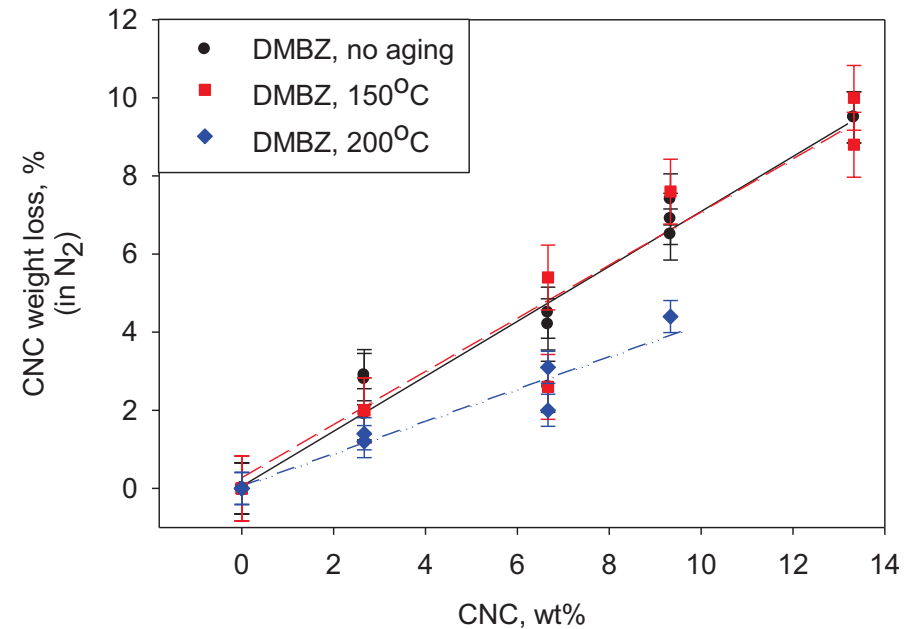




# Aging Study: CNC diminishes at 200°C

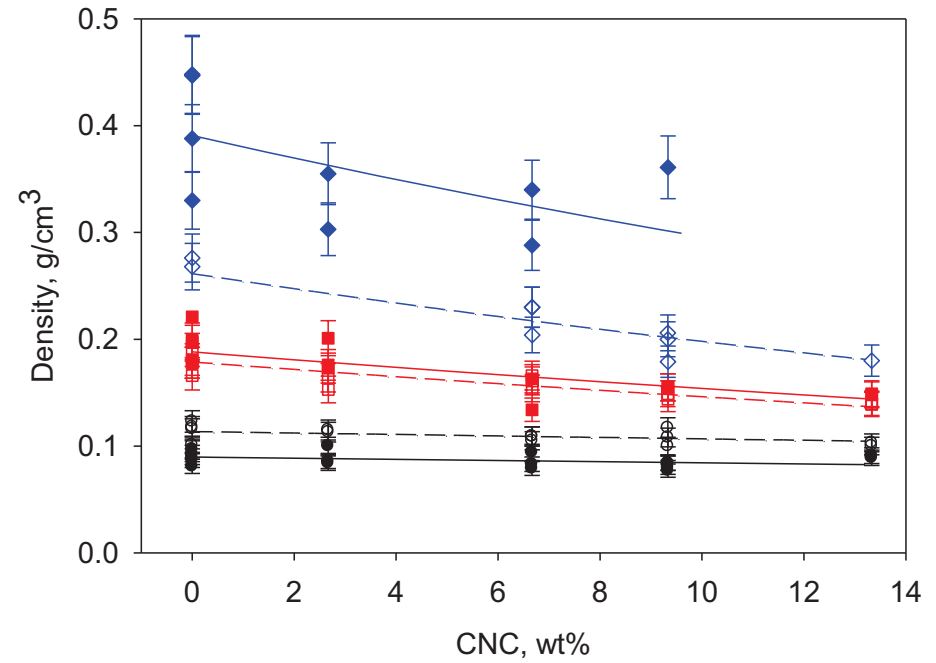
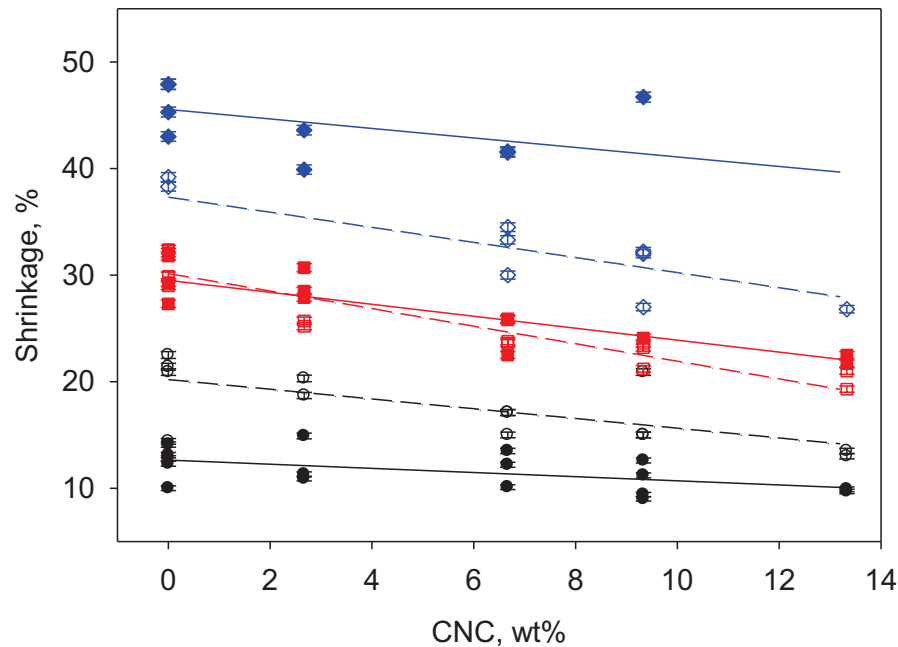


- Aged at 150°C for 30 h and 200°C for 24 h
- CNC is stable at 150°C for 30 h → no wt. loss during the aging period
- CNC starts to decompose at 200°C
  - Slowly diminishes over 24 h of aging
  - Higher decomposition rate at higher CNC content (less PI in the matrix composite)

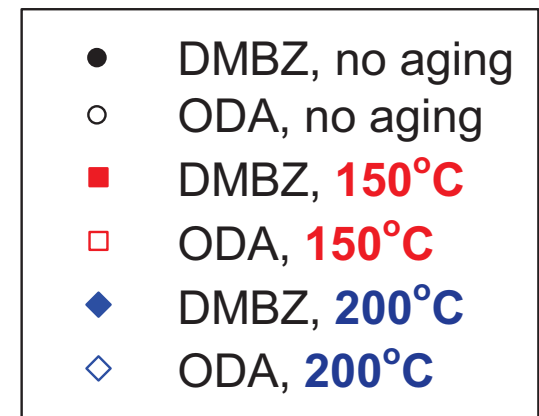




# Aging study: higher CNC loading reduces shrinkage and lowers density



- At higher CNC content → lower shrinkage and density
- At elevated temperature
  - higher shrinkage and higher density
  - Higher shrinkage and density for DMBZ-base aerogels





# Conclusion

## With the incorporation of CNC:

- Good CNC-polyimide interaction
- Retained pore size and structural integrity
- Improved both physical and mechanical properties

## At higher CNC loading:

- Lower shrinkage and density (both at RT and elevated temperatures)
- Higher porosity
- Lower BET surface area
- Little change in compression modulus
- Higher tensile modulus
- Lower % elongation

## More rigid backbone, DMBZ vs. ODA:

- Better physical properties at room temperature
- Physical properties suffered more at elevated temperature



# Acknowledgements

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