In-situ polymerization of polyaniline in veneers.

Effect on material conductivity, morphology, and flame retardance

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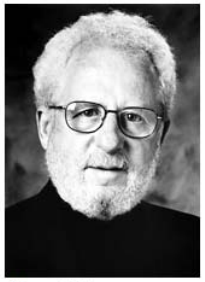
Conducting polymers

- Developed in the last 20-30 years


Alan J. Heeger


Alan G. MacDiarmid

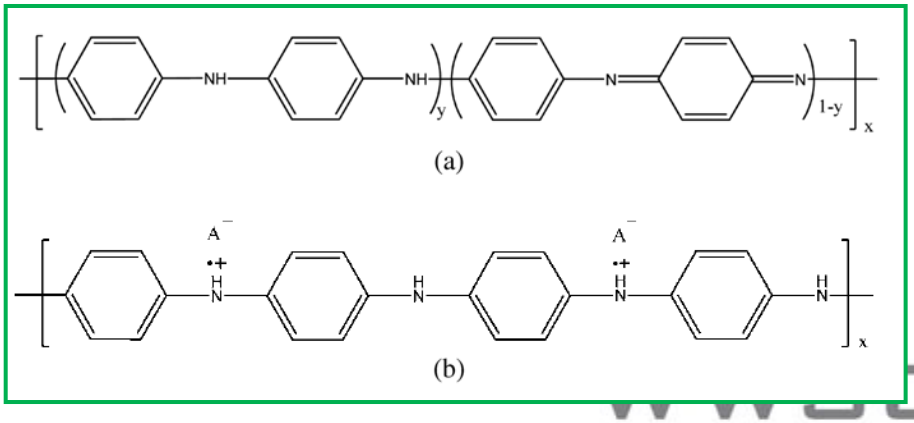

Hideki Shirakawa


The Nobel Prize in Chemistry 2000
Alan Heeger, Alan G. MacDiarmid, Hideki Shirakawa

Applications for conductive polymers

- O_2 sensors
- Inks for printed circuits
- Corrosion inhibitors
- Anti-static and conductive coatings
- Electrostatic dispersive coatings (ESD)
- Electromagnetic interference sheilding
- Waste water filtration of heavy metals

Emeraldine Salt: 50% oxidized and 50% reduced



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"The Nobel Prize in Chemistry 2000". Nobelprize.org. 22 Aug 2011 http://www.nobelprize.org/nobel_prizes

Conductive polymers on their own:

- Provide for a wide range of material applications

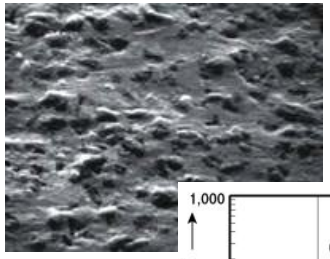
10^{-16} insulating 10^{-12} Anti-static 10^{-9} 10^{-7} Conductive (carbon part) 10^{-3} Conductive (carb/steel fibers) 10^{-1}

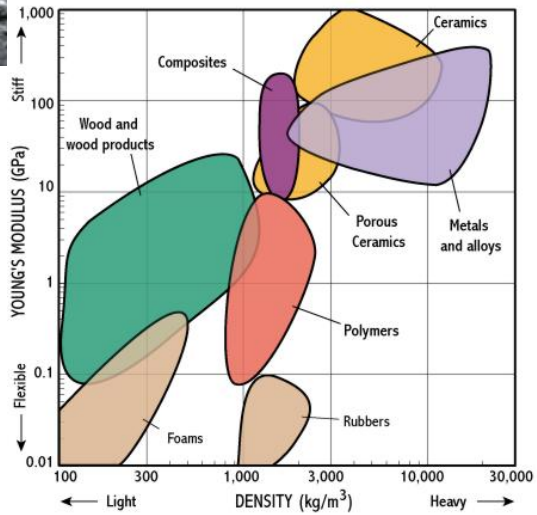
Conductivity →

  - Have little strength
  - Are brittle
  - Usually do not melt until after the degradation temp
  - Not soluble in common solvents

In polymer composites

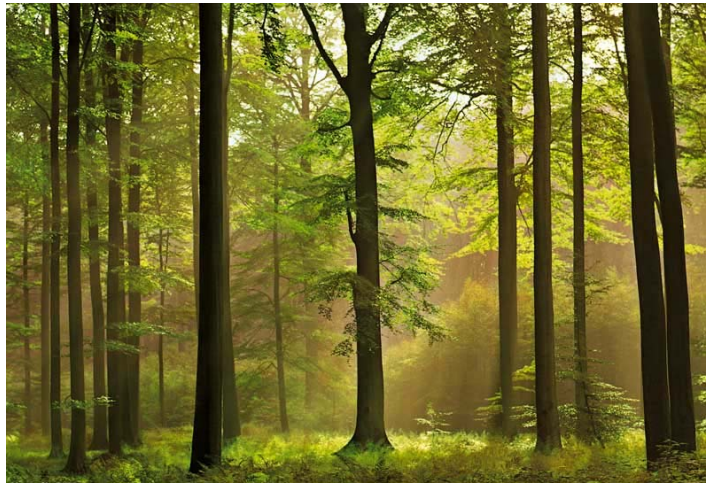
  - Creates ”shedding” of particles
  - Heavy materials
  - High loadings needed for conductivity
  - Decreased polymer matrix properties
  - Composite recycling is less favorable

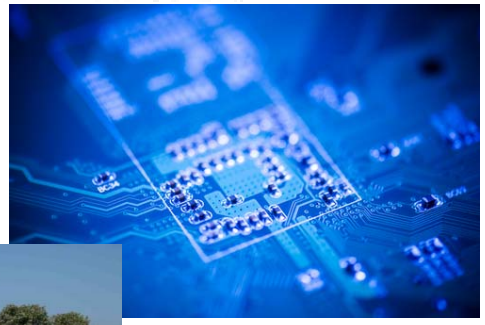




Aim

To use the complex structure of wood as a template that is by nature a light yet strong material and modify with organic conductive polymers in order to obtain a novel functional material.





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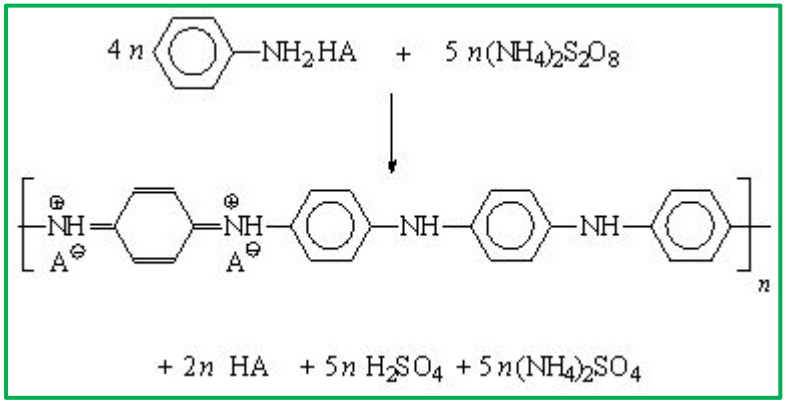
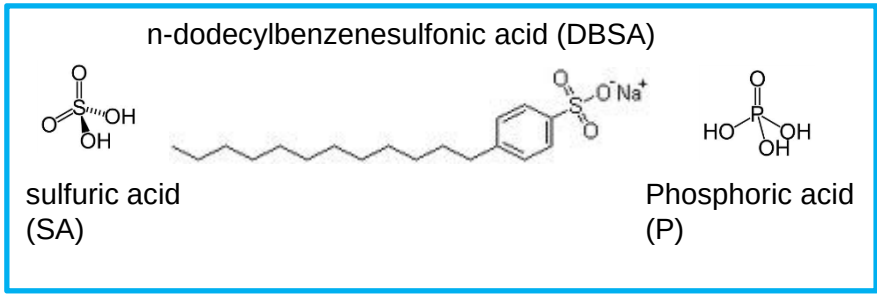
Fabrication of conductive veneers

- Southern Yellow Pine veneers of 0.6 mm in thickness
- Vacuum pressure impregnated at 0ºC for 24 h at 10 bars under inert atmosphere (N_2)
- Oxidizer: peroxydisulfate/aniline ratio of 1.25
- Dopant: 1:1 dopant:aniline molar ratio
- pH around 1 for doped solutions
- Undoped polyaniline formulation as blank



Variables

- Concentration in water: 0.2, 0.1, and 0.05 M solution of aniline in water
- Dopant: Different counterions (SA, DBSA, P)



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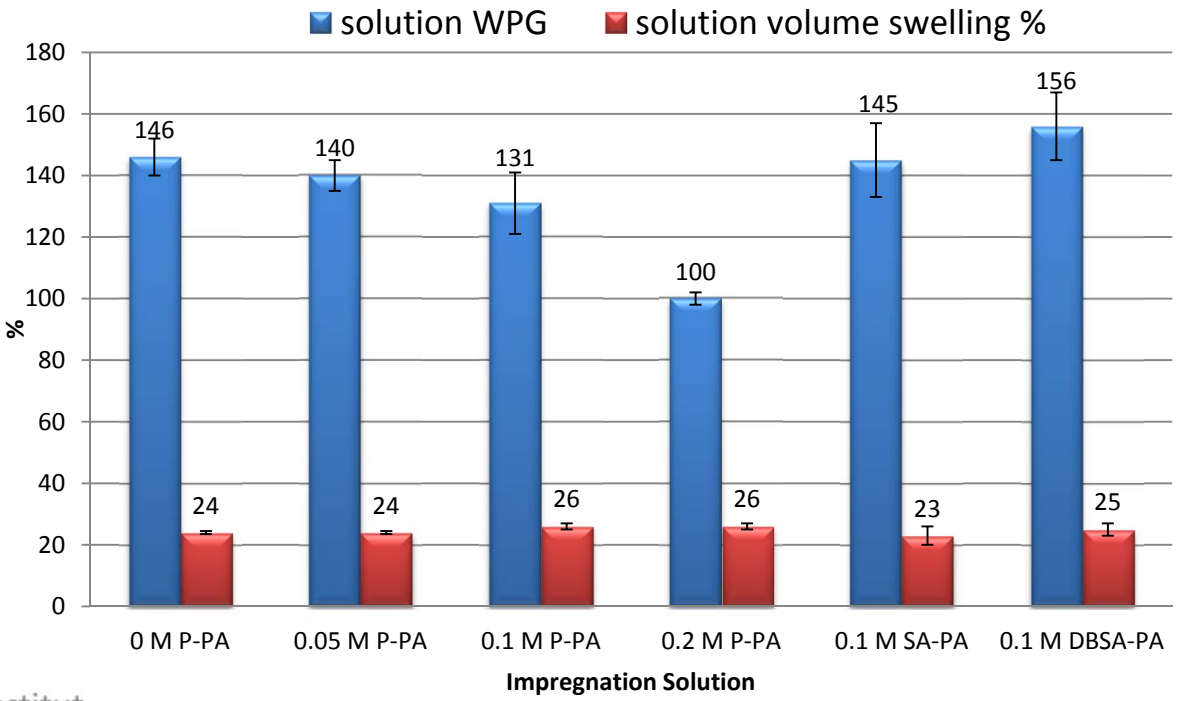
How did the impregnation solutions interact with the wood?

How much solution did the veneers take up during impregnation?

Like a dry and wet dish sponge? ⟶

- Decreased wet WPG with higher concentrations of PA
- Water is a good carrier solution
- No difference in volume swelling observed



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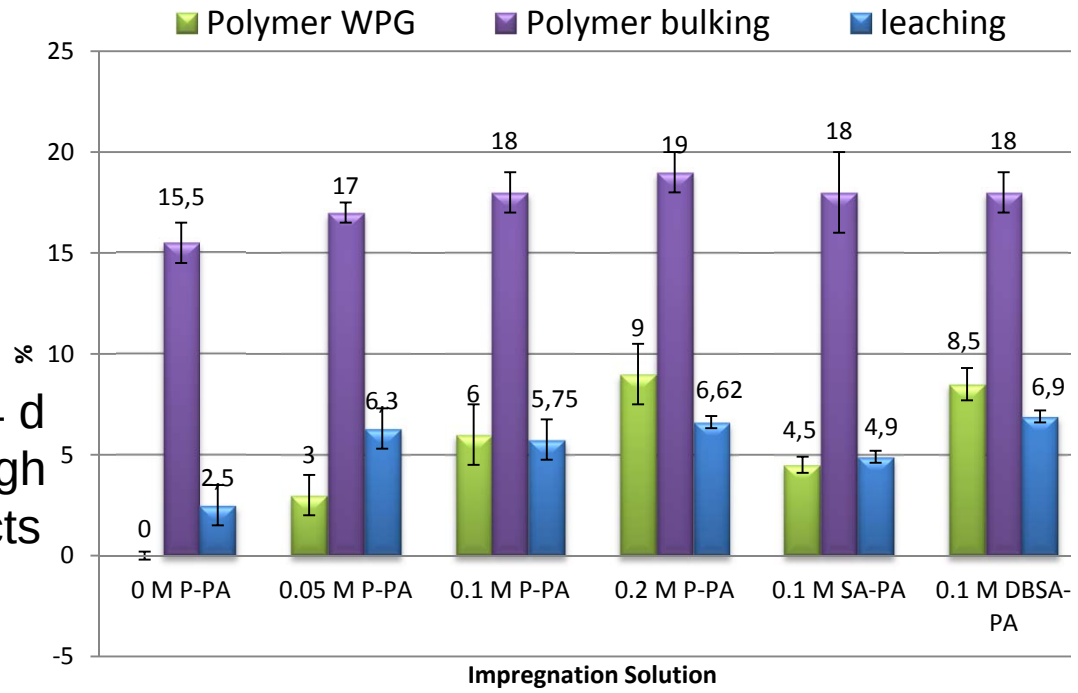
How much polymer was absorbed by the veneer (dry WPG)?

Did polymer go in the cell wall (bulking) and was it just retained (leaching)?

- Dry WPG of polymer was 3-9 wt%
- Slight polymer bulking is observed
- Weight loss after soaking in water 14 d
  - Leaching was observed to be high
  - Hemicellulose and rxn bi-products



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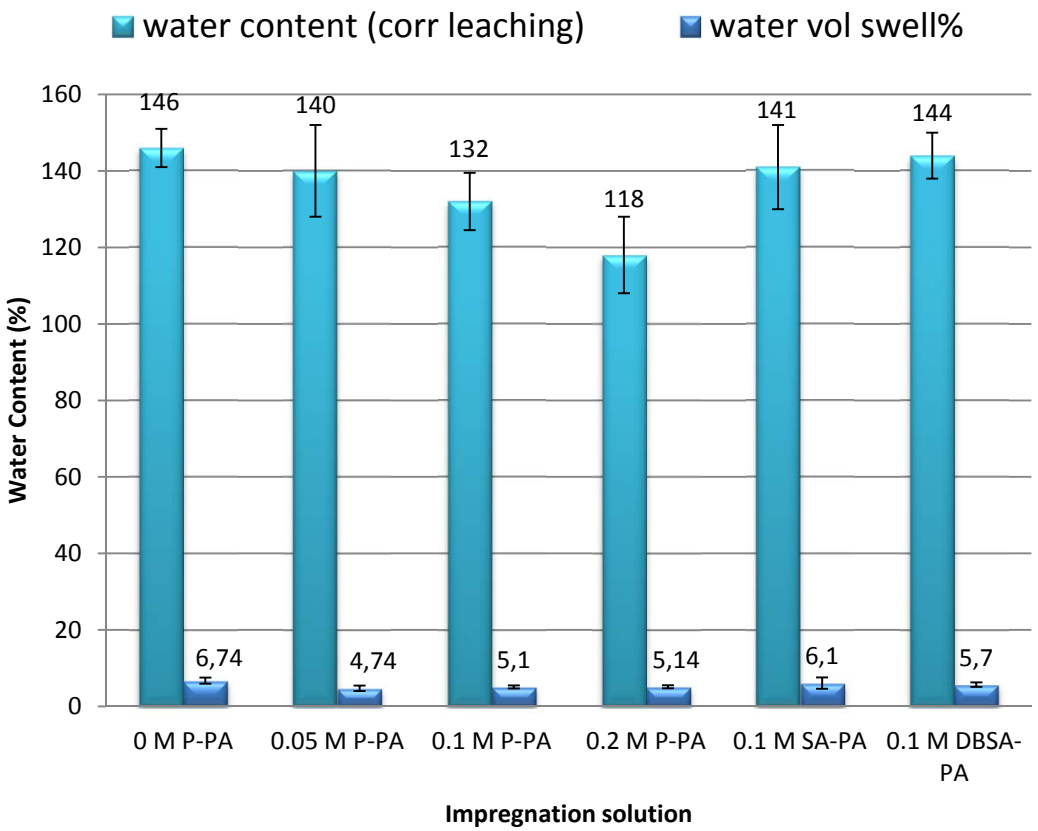
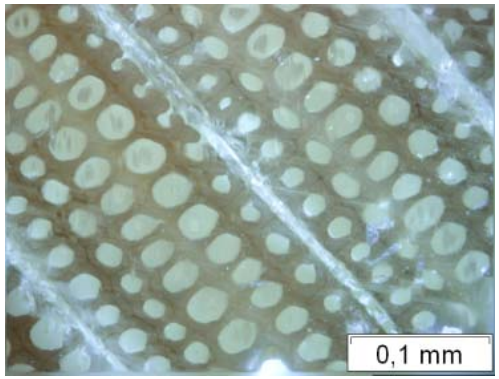
How does polymer modification effect water sensitivity of the veneers?

- 14 days of soaking in water (EN-84)
- Polyaniline veneers take up less water
  - Polymer bulking the cell wall
- volume swelling
  - 30% reduction in P-PA
  - Better dimensional stability



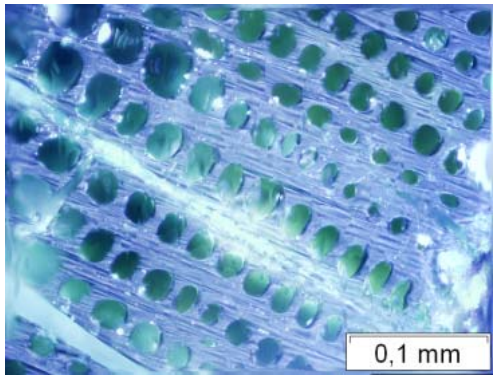
Observation of veneers

Polymerization in veneers was achieved!
- along with free polymer particles in water

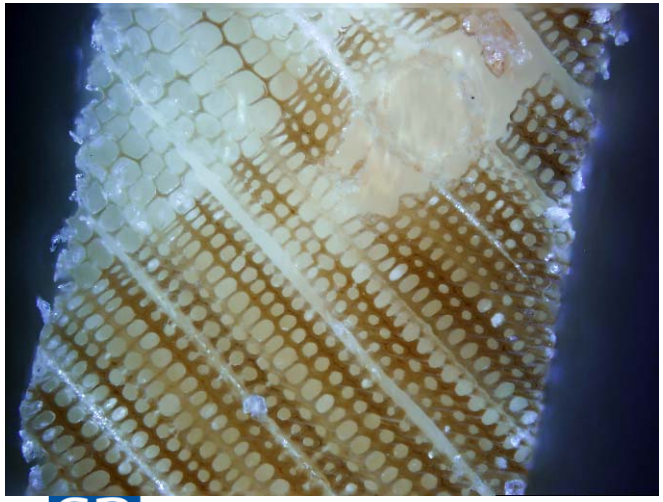


unmodified

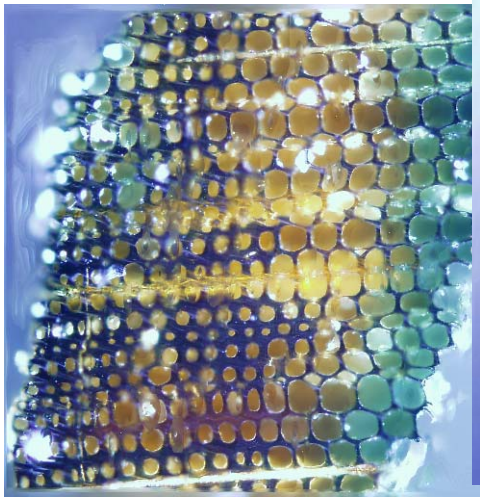
- Obvious color change
- No lumen filling
- Difficult to tell in which part of the structure is most favorable
- Appears homogeneous



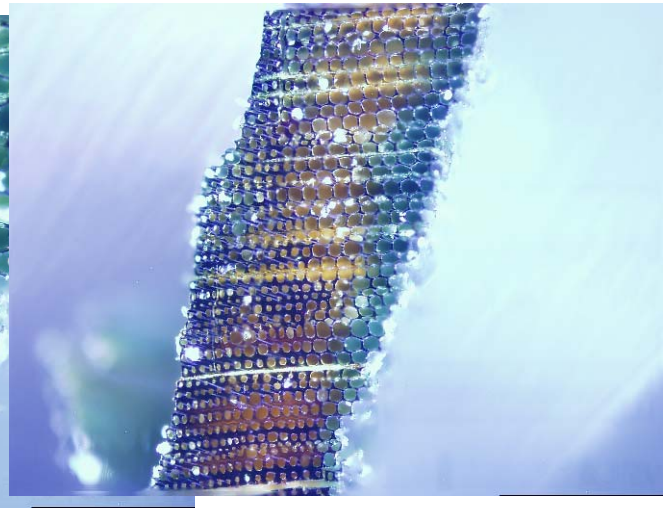
0.1 M P-PA



unmodified



0.1 M DBSA-PA

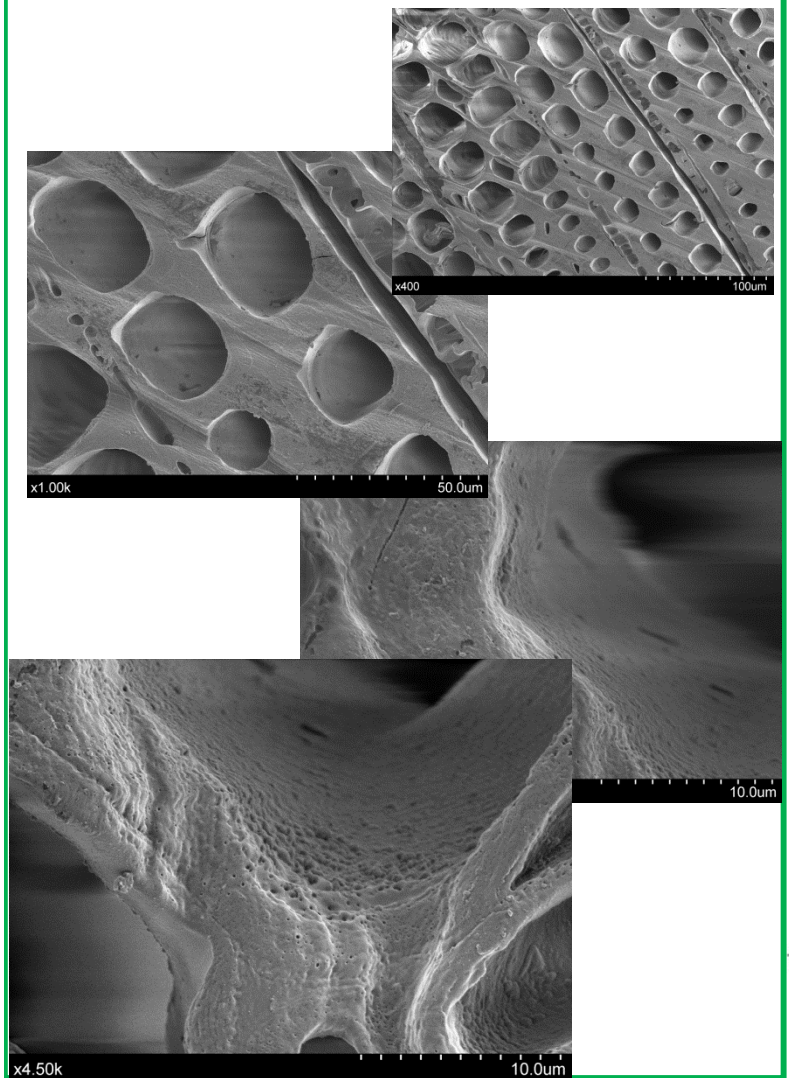


0.1 M SA-PA

Choice of dopant does not seem to hinder diffusion

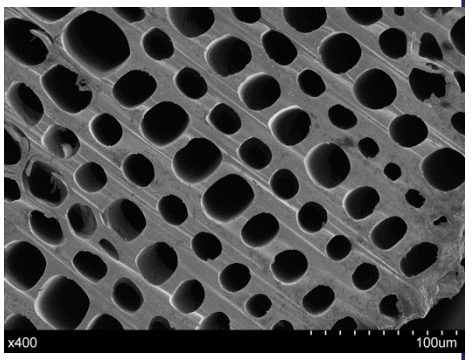
Unmodified SYP veneer

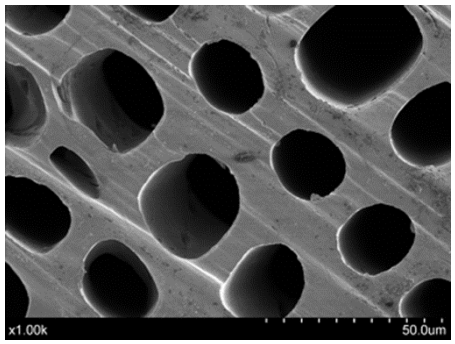
- Clean textured surfaces observed

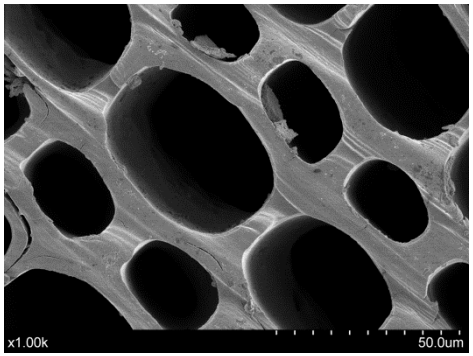


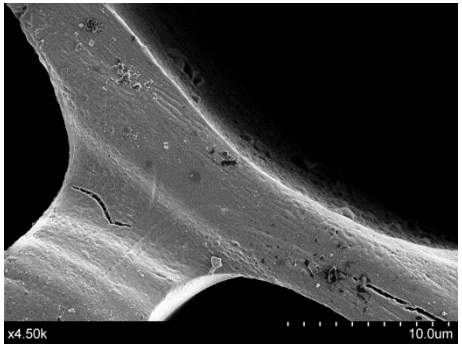
0.2 M Polyaniline phos doped

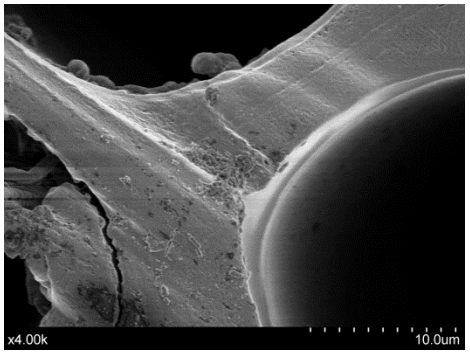
-No lumens filled
- Small particles observed
  - Darker spots in cell wall
  - Particles on inner cell wall



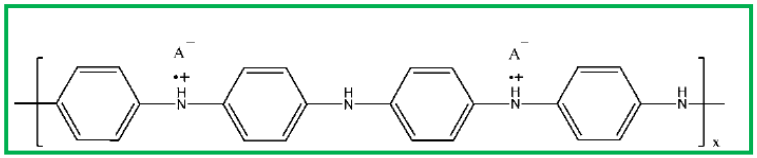




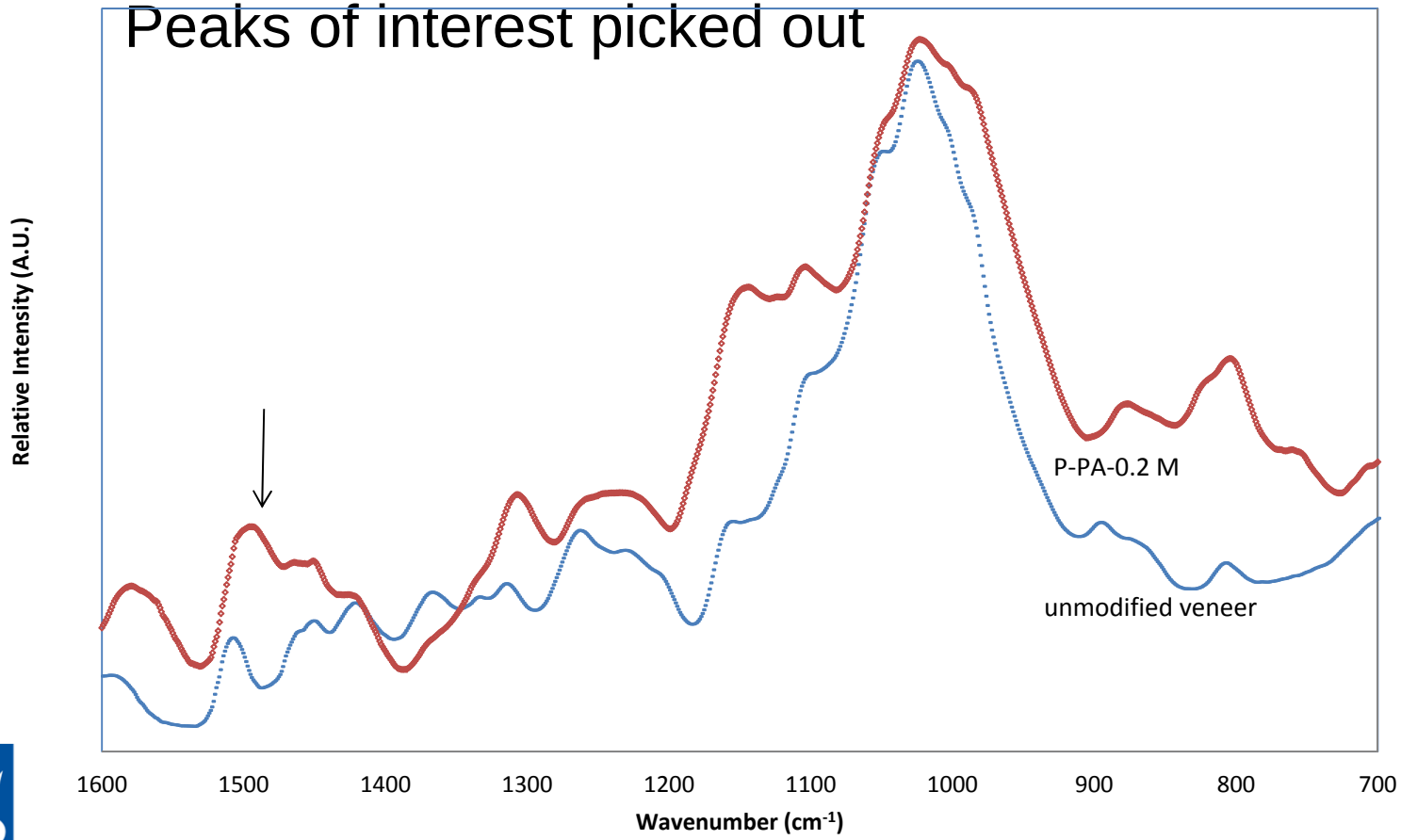




FT-IR Mapping



Peaks of interest picked out



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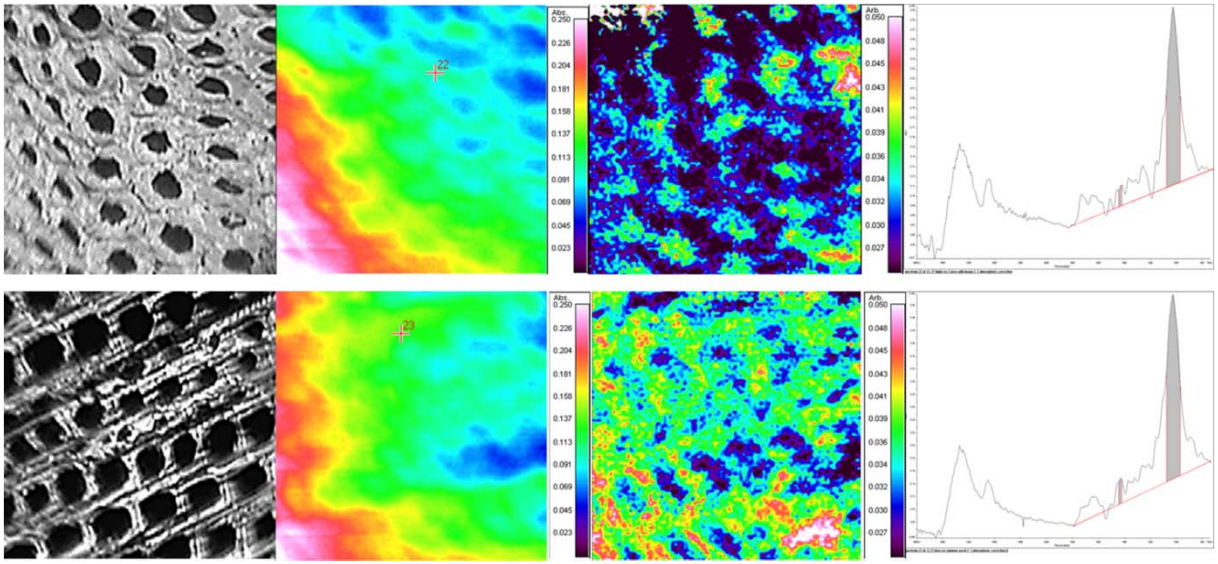
Mapped by FT-IR imaging

Unmodified veneer

0.2 P-PA veneer



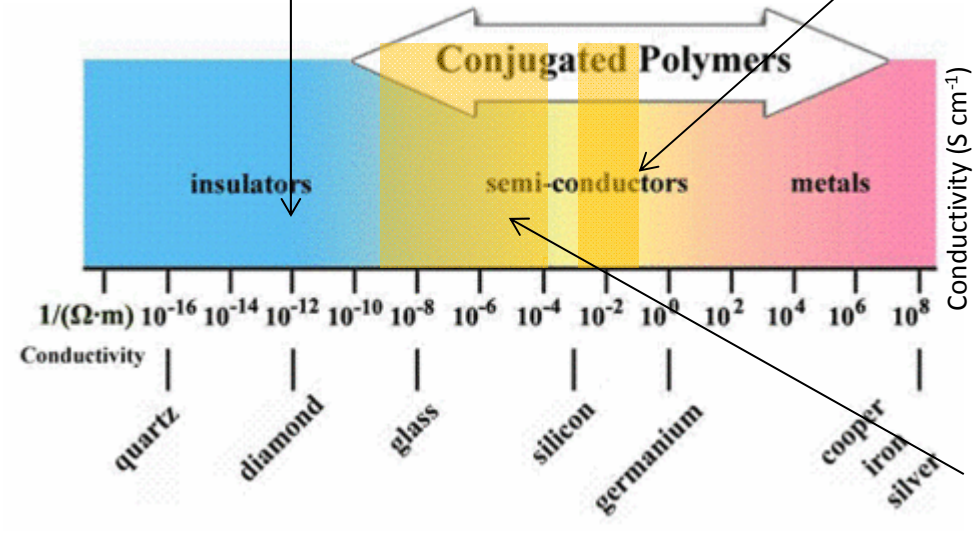
- The homogeneous distribution of polyaniline is observed
- Higher concentrations in the middle lamella

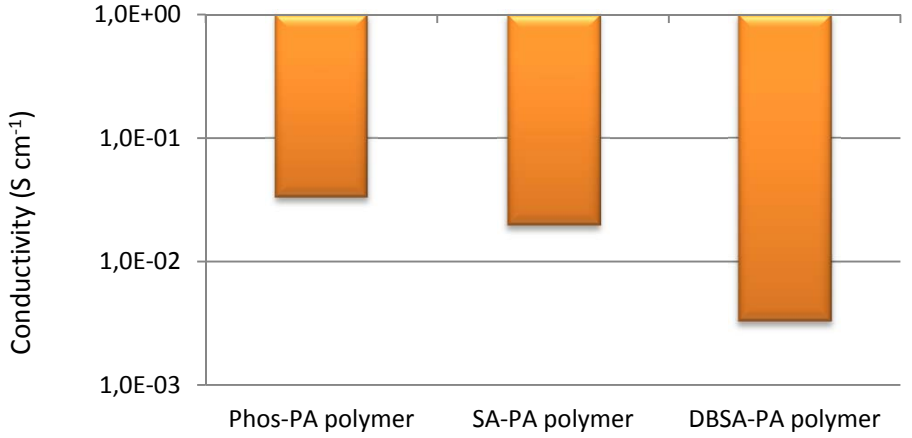
Are the modified veneers conductive?

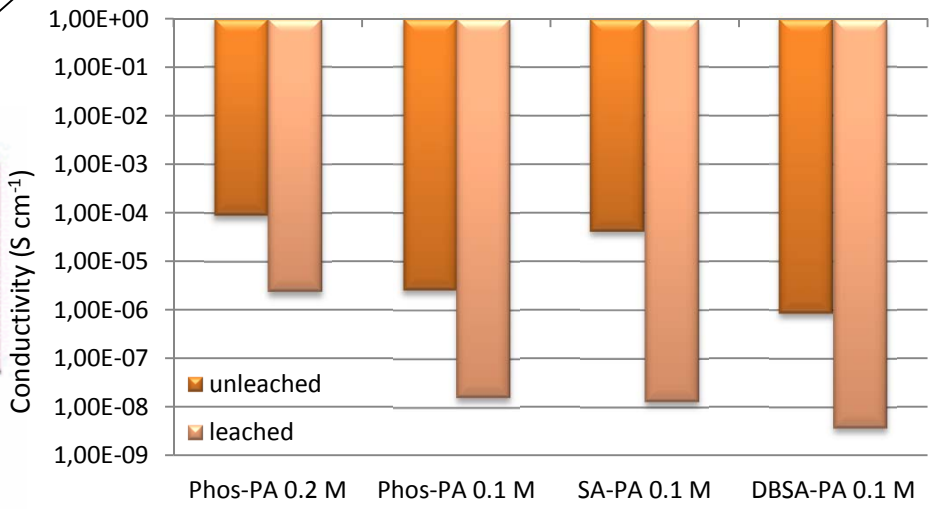
Measured with a four point probe

- On either side of sandwiched veneer

Sample	1/ρ (S cm-1)
Untreated wood	7 E-12
Phos-PA 0.05 M	1.4 E-12



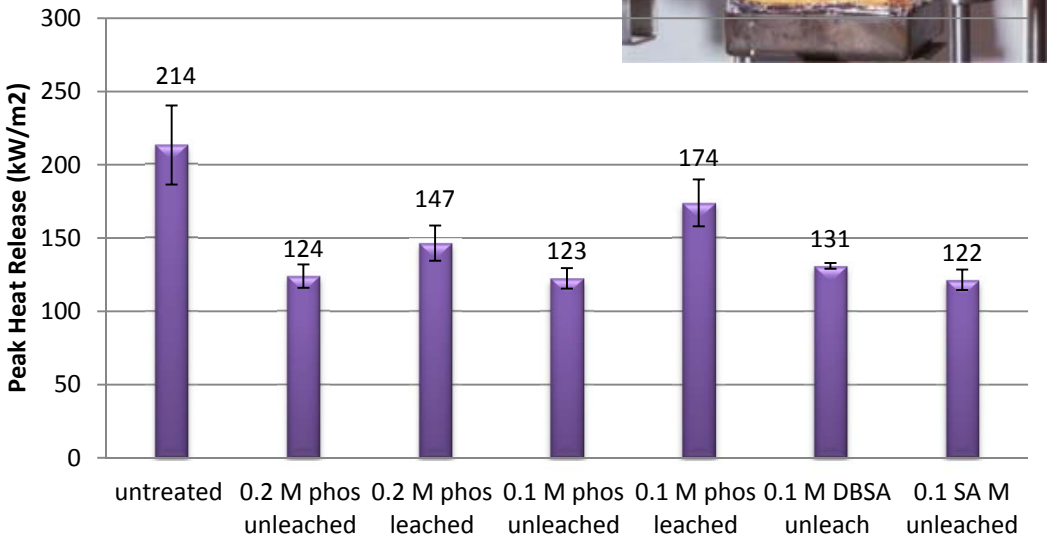


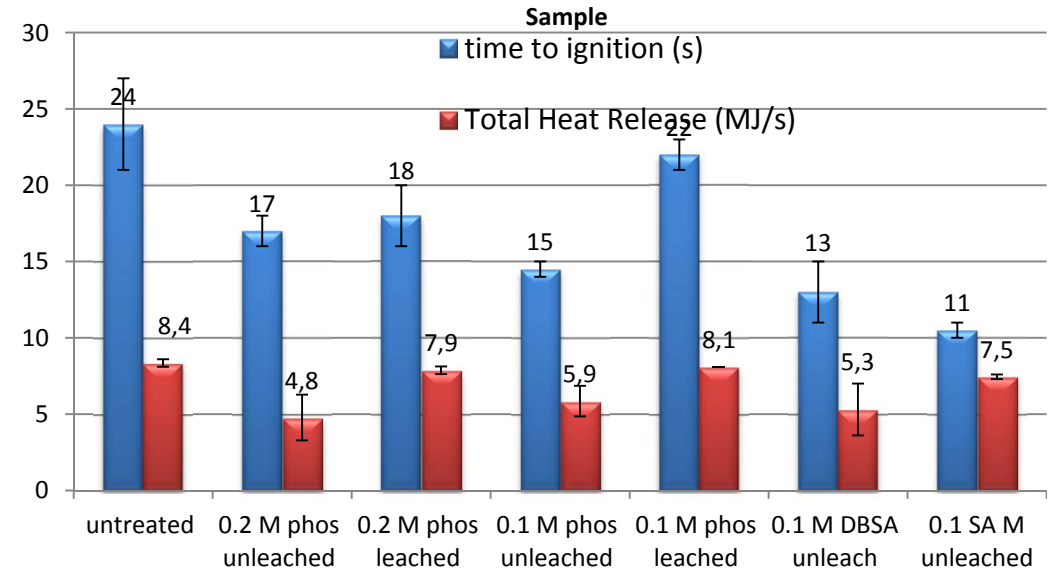


10^{-4}-10^{-9}!
Large range of material applications in conductive and anti-static range

Flame retardance?

- Modified veneers measured by cone calorimetry
  - Peak and total heat release= lower
  - Time to ignition= shorter!
    - More hydrophobic
    - Dryer samples





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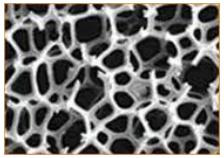
Summary

- Production of conductive veneer is feasible

- Large range of conductivity (10^{-9} - 10^{-4} S cm^{-1}) so that a large number of material uses is possible!

- Polyaniline does not fill the lumen and thus many benefits are obtained without the additional unnecessary weight



- Improvement in wood fire retardancy and water sensitivity
  - Large potential for:
    - Anti-static building materials
    - Broad array of technical applications

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Mats Westin

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Shadi Jafarzadeh


Jinshan Pan

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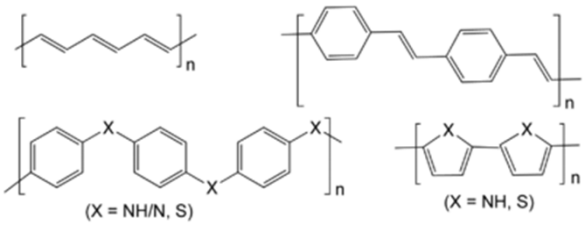
Thanks for listening

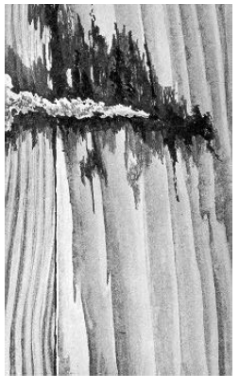
Questions and discussion are welcome!

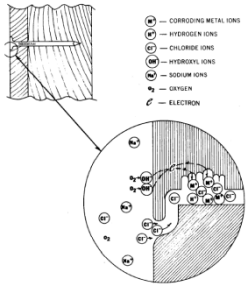
Next steps



- Other conductive polymers that are not as popular as polyaniline

- Different types of wood and weathering with polyaniline treatments





- Corrosion resistance with different types of metal in contact with the treated wood

- Incorporation into devices?

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DEGRADATION OF WOOD BY PRODUCTS OF METAL CORROSION

U.S.D.A. FOREST SERVICE RESEARCH PAPER

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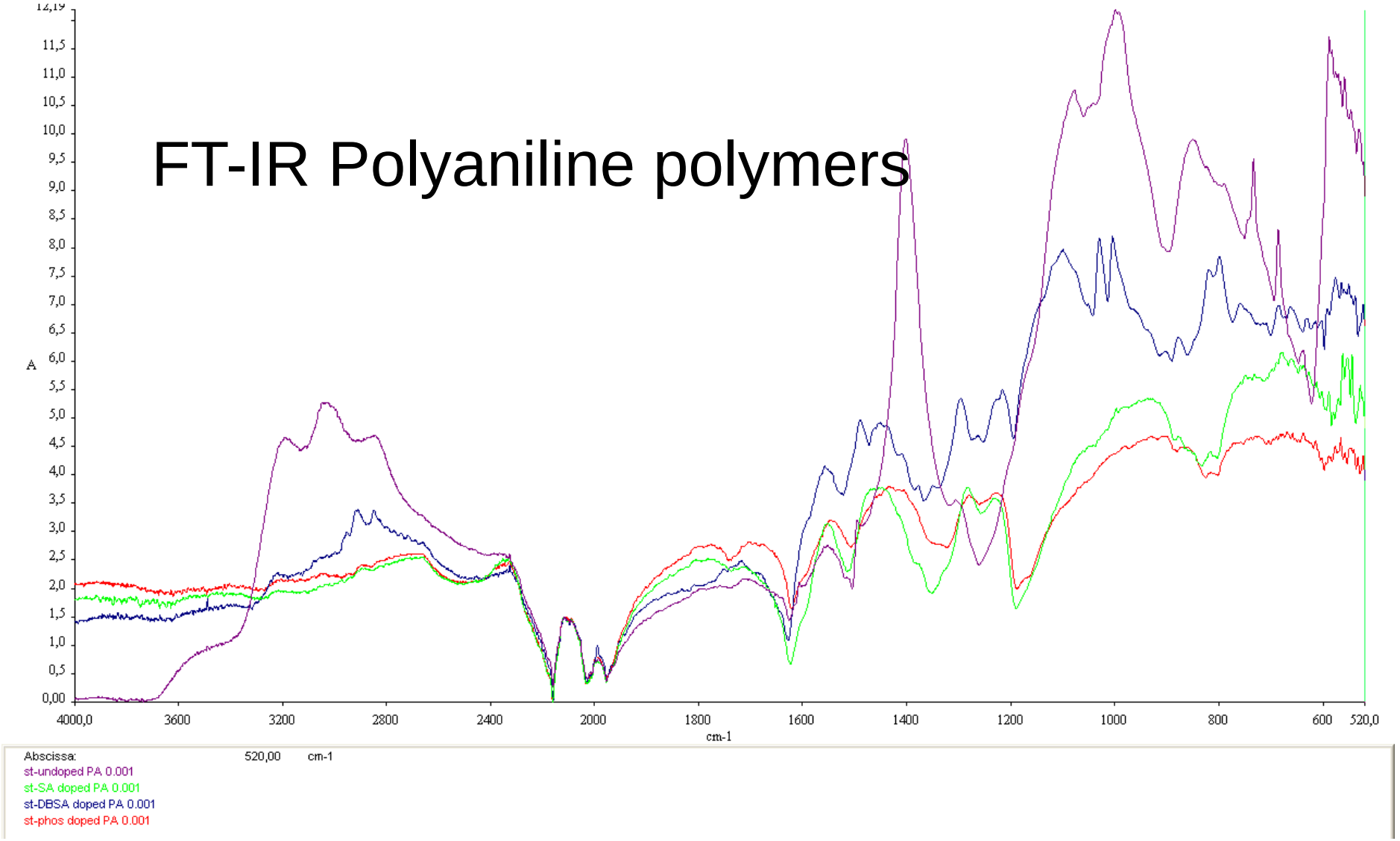
FT-IR Polyaniline polymers



Why is polyaniline conductive?

- Conductivity involves the migration of a proton
  - ”polaron (radical cation) hopping mechanism” has been proposed
  - 2 factors influence conductivity
    1. degree of oxidation (electrochemical doping)
    2. degree of protonation (acid doping)

  - Anion present has an impact on:
    - Conductivity, material propertis, molec. structure

Polaron Migration