Potential for Biobased Adhesives in Wood Bonding

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History of biobased adhesives – main component

- **Ancient**
  - Animal glues (collagen) from hides and bones
  - Blood
  - Paints – egg whites and milk
  - Pitches for sealant adhesives

- **Up to 1700**
  - Casein from milk
  - Fish (collagen)

- **1700-2000**
  - Commercial adhesives
  - Highly alkaline soy flours
  - Honeymoon soy-RF
  - Tannin

- **2000’s**
  - Slightly basic soy flour with co-reactant
  - Soy with magnesium oxides
Additive role (extender, modifier, filler)

- Proteins
  - Wheat gluten, soy, blood
- Tannin with PF
- Lignin
- Walnut shell flour, etc.

Not considering urea and formaldehyde since they are made synthetically, although they can also be biobased
Casein glulam - FPL 1935 to 2010
What makes bonding wood hard?

- Complex surface structure that varies greatly from location to location (density, moisture content, cellular fracture, rays, reaction wood, juvenile wood, etc.)
- Many wood species are used, but they have significantly different structural properties and extractive chemicals
- Properties of surface vary rapidly with time (contact angles and extractives) leading to decreased bond strength
- Moisture durability required in most cases, which changes the wood’s dimensions
- Creep resistance, often under significant load, requires the use of thermoset adhesives
- Temperature durability required in some cases (roof deck, attic, fire)
Moisture durability

- Changes in moisture causes the wood to swell and shrink
- The bonded portion needs to accommodate the dimensional changes or failure will occur

Internal forces in addition to applied forces
Response of the adhesives to wood swelling

In-situ polymerized, infiltrate cell wall to reduce swelling

Pre-polymerized, need right flexibility to flex but to not creep
Adhesive classes

In-situ polymerized – phenolics, amino resins, epoxies, pMDI

Pre-polymerized – polyurethanes, poly(vinyl acetate), EPI, proteins
Typical wood surfaces
Why adhesive interaction with wood is important

Lumen filling does not reduce impact of swelling

Cell wall infiltration reduces swelling and its impact
How do biobased materials fit into these adhesive classes?

- Tannins and lignins are *in-situ* polymerized
  - Thus need to infiltrate cell wall to reduce swelling
- Proteins, oil-based polyurethane, and carbohydrates are pre-polymerized
  - Need flexibility as well as strength
- Biobased additives generally do not enter the cell wall and usually change the properties of the adhesive on the surface

Condensed tannins structure model
Condensed tannin – PF adhesives

- Tannin structure has many available reactive phenol groups
  - Including resorcinol type groups giving it high reactivity
- It has significant molecular weight and thus is unlikely to infiltrate the cell wall
- Limited availability makes it useful only in certain locals where PF is less available and more expensive
- Used commercially
Condensed tannin (non-PF) adhesives

- Formaldehyde
- Urea-formaldehyde
- Hexamethylenetetramine
- Methylolated aminoparafins or methylolated nitroparafins
- Acid or base self-condensation
Lignin structure (generalized model)
Lignin sources

- Sodium hydroxide pulping of wood
- Sulfite pulping of wood
- Complete acidulation of Kraft black liquor (50,000 ton/year)
- Partial acidification of Kraft black with carbon dioxide (70,000 ton/year)
- Organosolv pulping of wood or grasses
- Biofuel ethanol production by product from wood or grasses (6 projected plants using corn stover, DDG, corn cobs and bagasse)
Lignosulfonate structure
The largest volume for lignin is lignosulfonates
Originally produced from bisulfite pulping of wood
Now also produced by sulfonating Kraft lignin
Lignin contains varying degrees of sulfonation
Markets for about 1 million tons/year include:
  - Dispersant for concrete admixtures
  - Animal feed binder
  - Oil well drilling mud
  - Dust control for road work and mineral mining
  - Many minor applications as surfactant, including PF adhesives
Lignin uses

- Largest current demand is for lignosulfonate
- Market reports
  - Frost and Sullivan (2012) projects $130 Bn/yr market
  - Lux Research (2014) projects $242 Bn/yr market
  - This would be equivalent to about 186 Million/tons on average
  - However, these projections seem overly positive with current plans for lignin utilization
Lignin-phenol-formaldehyde adhesives

- Many papers have shown that a wide variety of lignins can replace up to 40% of the phenol in Pf resins, with the usual amount in the 20-30% range, especially if methylolated first.

- There are reports that lignin was at one time used in PF resins.

- Today there does not seem to be any lignin used in PF resins in the US or Europe.

- Why lignin is not used
  - Slow curing makes it more of a filler than an extender.
  - No real incentive for PF manufacturers to complicate their process, especially since PFs are already specialty products.

- Need development work to make LPF more viable.
Other lignin adhesives

- Lignin with hydrogen peroxide
- Enzymatically activated lignin
- Methylolated lignin with polymeric diphenyl methylene diisocyanate
- Lignin glyoxal
- Tannin-lignin-formaldehyde adhesive
Other potential lignin markets

- **Functional Fillers Polymeric Composites**
  - RecycleWood uses lignin at 25-30% loading to make compostable garbage bags

- **Asphalt Emulsifiers**
  - Lignin-polyamine condensates can make 70% asphalt emulsions

- **Polyurethanes**
  - Lignin can partially replace polyols to make stiff PU foams for insulating panels

- **Wastewater Treatment Polymers**
  - Lignin can be cross-linked to form effective flocculants

- **Carbon Fiber**
  - WHEN successful, this will be a HUGE market for lignin
Protein adhesives

- Most of the research has been on their properties in food applications, which has some relation to adhesives.
- However, the problem comes in that protein properties are very dependent upon processing and the protein used in individual studies is usually quite vague.
- For most grain and oil seed proteins, the proteins are globular and therefore colloidal properties are very important.
- Work on chemical modification has been good, but it lacks understanding of real protein properties.
- Interesting work on the properties of adhesives used by sea creatures.
- More potential in proteins than has been unlocked so far.
Wood-derived adhesives

- Besides wood components being used in adhesives,
  - Liquidified wood or bark
  - Biooil
  - Biochar
- These are often used in PF adhesives
Tree and plant oils

- Epoxidized oil resins for use in polyurethanes
- Acrylic epoxidized soy oil resin
- Transformations include epoxy, carboxyl, hydroxyl, vinyl, amine, etc.
Thank you for your kind attention

Questions?