Using DDGS-Soy Flour Mixtures as Adhesives for Wood Composites

Brent Tisserat and Veera Boddu

Functional Foods Research Unit & Plant Polymer Research Unit, National Center for Agricultural Utilization Research (NCAUR)

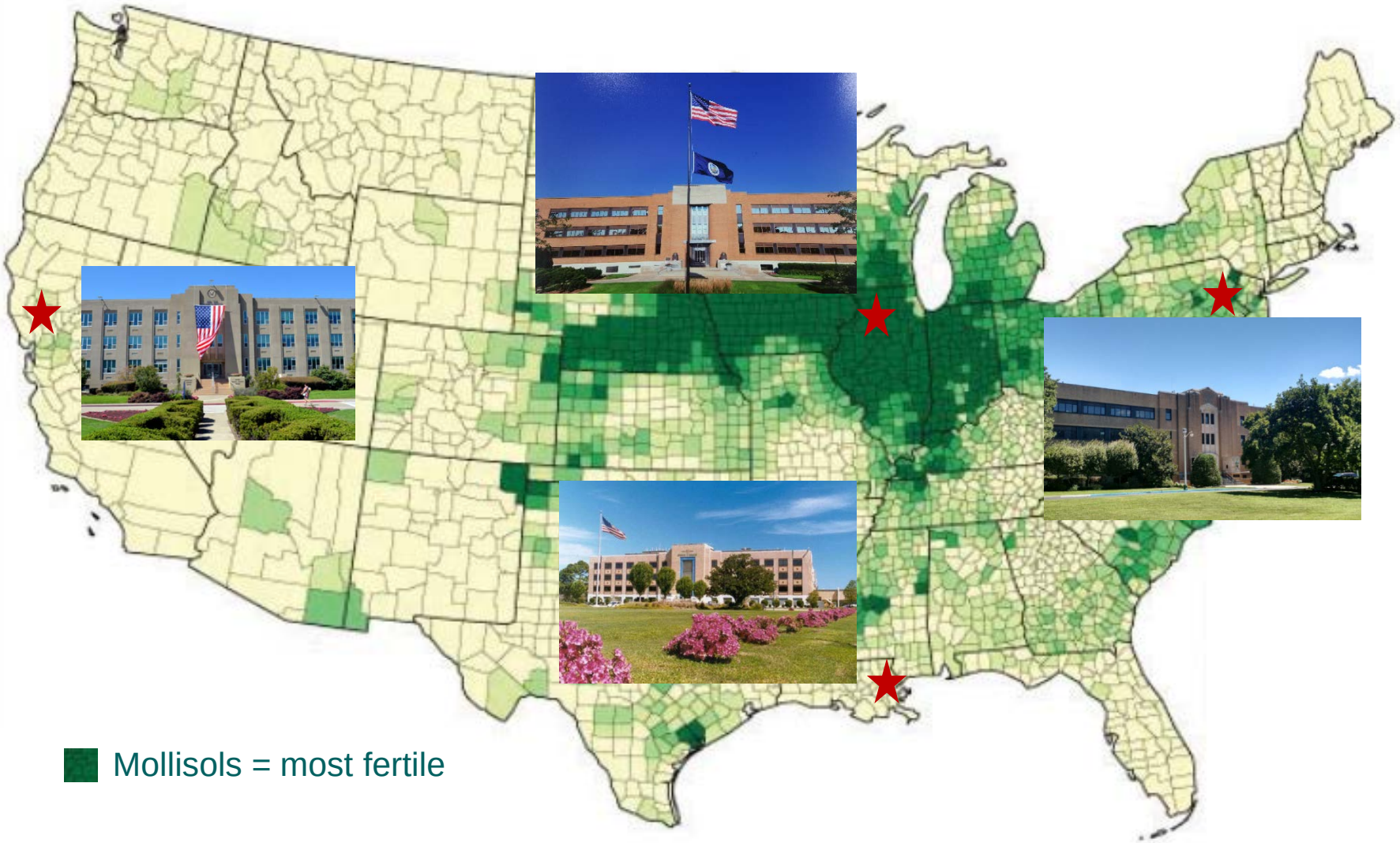
Agricultural Research Service, US Dept. of Agriculture

(USDA-ARS) 1815 N. University St., Peoria IL 61604 USA

ISBBB-2018, S11.1, July 25th, 2015; 8:30-8:55AM

Science Based, Farmer Focused, Citizen Supported Research

USDA
Agricultural Research Centers



National Center for Agricultural Utilization Research (NCAUR)



- Formerly, USDA Northern Regional Research Center
- 270,000 sq. ft. (25,000 m^2)
- 255 FTE research staff
- 97 Ph.D. scientists
- 7 research units
- 36 national priority projects
- $33 million budget
- 200+ patents since 1980
- International network of research collaborations

1. Bioenergy Research (BER)
2. Bio-Oils Research (BOR)
3. Crop Bioprotection Research (CBP)
4. Functional Foods Research (FFR)
5. Mycotoxin Prevention and Applied Microbiology (MPM)
6. Plant Polymer Research (PPL)
7. Renewable Product Technology Research (RPT)

Science Based, Farmer Focused, Citizen Supported Research

NCAUR - Research Focus

Develops bio-based products from agricultural commodities that can compete with products using non-renewable resources.







NCAUR - History of Commercial Impact

- Penicillin
- Dextran
- Xanthan Gum
- High Fructose Corn Syrup
- Baby diapers/super absorbents
- Corn-Soy Milk
- Soy-based Products
- …













Wood Products and the Demands

- **Annual per capita wood consumption (both developed and developing countries) is ≈0.5 m^3 per person.**
- **80% of wood consumption in developed countries is industrial or engineered wood products while in developing countries 80% of the wood is burnt as fuels.**
- **By 2030 global consumption of industrial as well as solid wood will rise by 60% over current levels and is predicted to continue to increase through 2060.**
- **This demand will put continued pressure of the Earth's forests which are already in serious decline.**

- Source: Food and Agriculture Organization of the United Nations (FAO) (2002). "Towards sustainable forestry," in: *World Agriculture: Towards 2015/2030 Summary Report*, (www.fao.org/3/a-y4252e.pdf), Accessed 01 July 2017.

Engineered Wood Products (Panels)

- Wood strands, particles, fibers, or veneers or boards of wood, fixed together with adhesives.
- They are engineered to precise design specifications.
- Are from scraps and wastes.
- Includes: OSB, Plywood, Particleboard, MDF & HDF



Uses of Various Wood Products

Primary Products	Uses
Sawn wood (planks, beams, lumber, rafters)	Furniture Home and industrial construction
Panels (plywood, veneer sheets, particleboard, fiberboard)	Home and industrial construction Manufacture furniture and cabinetry
Pulpwood	Printing, writing paper, paperboard, cardboard, newsprint, tissues, diapers
Biomass	Energy

Types of adhesives used in engineered wood include:

- Urea-formaldehyde resins (UF) most common, cheapest, and not waterproof.
- Phenol formaldehyde resins (PF) yellow/brown, and commonly used for exterior exposure products.
- Melamine-formaldehyde resins (MF) white, heat and water resistant, and often used in exposed surfaces in more costly designs.
- Methylene diphenyl diisocyanate (MDI) or polyurethane (PU) resins very expensive, generally waterproof, and does not contain formaldehyde.

Several of these adhesives contain formaldehyde which is a health (cancer) concern.



Sources: U.S. Consumer Product Safety Commission (CPSC) (2013). *An Update on Formaldehyde* (Publication 725. 2013 Revision 012013) ClassAction.org. (2015) & "Lumber liquidators class action lawsuit investigation over formaldehyde levels"

What about Natural Protein-based Adhesives? Where did they go?

- Soy protein-based adhesives derived from soybean meal (80 years ago).
- Soybean proteins are abundant, renewable, and biodegradable.
- Soybean meal originally was recognized as easy to handle.



However, soy protein adhesives were replaced in the 1960s by synthetic adhesives. In recent years, interest was renewed in them as adhesives because they were biodegradable and free of VOCs. Soya protein isolate is recognized as having high adhesion strength but actually costs more than phenol-formaldehyde and urea-formaldehydes. However, Soybean flour is too expensive to be used in engineered wood products and instead is employed as a food additive.

Cost is the major problem in using bio-based adhesives

- Although soya flour is recognized as an important bio-based adhesive there is a great need to develop less expensive, abundant bio-based adhesives to manufacture engineered wood products.
- This presentation addresses this problem by employing a low-grade by-product obtained from dry mill corn processing, namely Distiller's Dried Grains & Solubles (DDGS) blended with Soy flour.

Economics of Raw Materials to Use as Adhesives/resins (Prices provided by Alibaba.com)

Material	Protein (%)	Cost ($/lb)	Cost ($/kg)
Soybean	45-50	0.45-.50	0.99-1.10
Zein	90	4.54-18.20	10.00-40.00
Corn Gluten	55-70	0.36-0.45	0.79-0.90
DDGS	27-40	0.03-0.05	0.06-0.10

Note: Soya Flour costs 10 times as much as DDGS.

Wood reinforcement materials cost ~$0.08-0.22 a pound (Clemons,C.M. 2010, Wood flour. In: Functional Fillers for Plastics, Chapter 15. 2nd Ed., Wiley-VCH, Weinheim, Pp. 269-290.)





• **Dried Distillers Grain & Solubles (DDGS)** are generated by distillation industry to make ethanol for biofuels by Dry Milling Corn.

• 42 million metric tones of DDGSs are produced annually in North America and the figure will double in the next few years

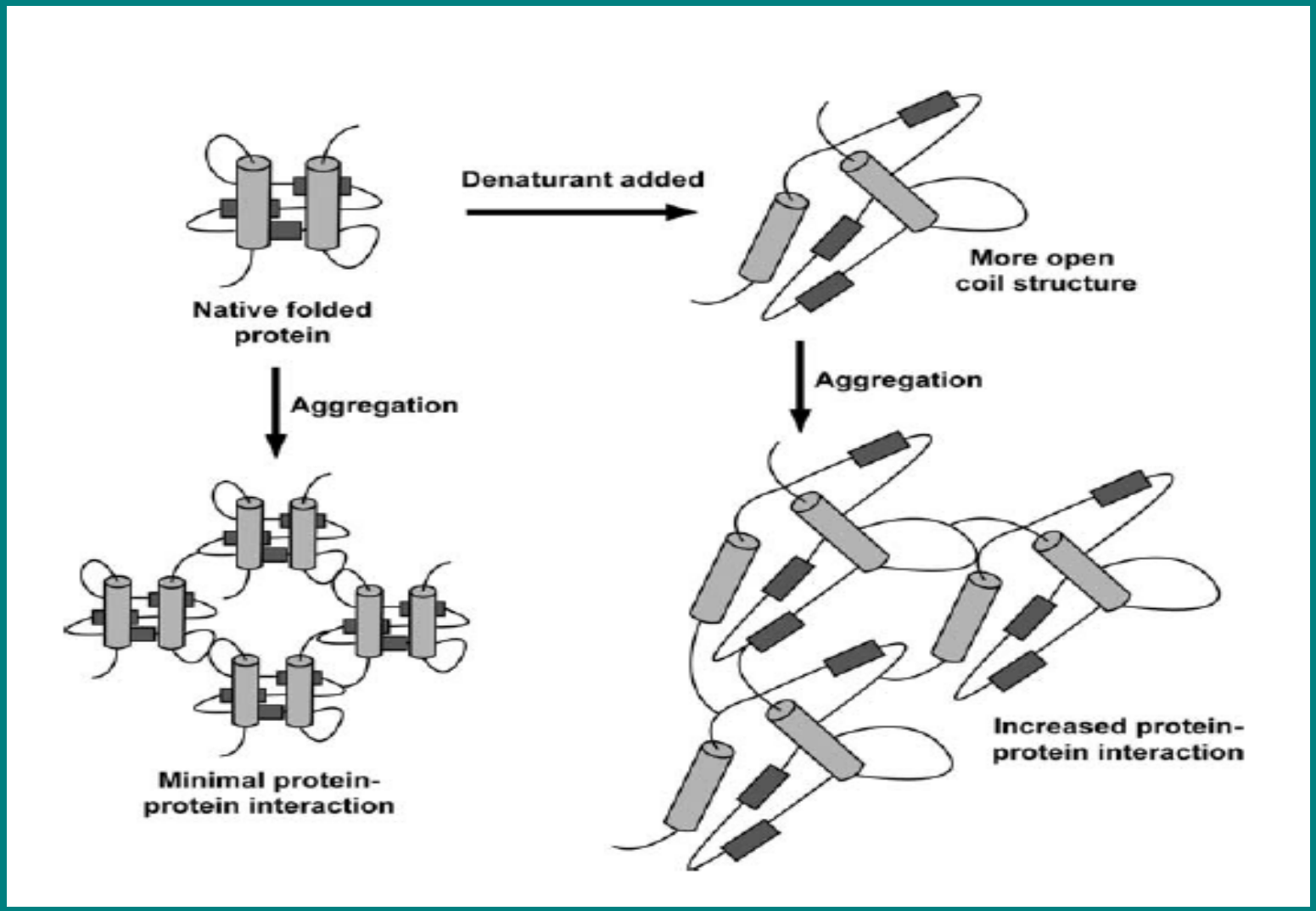
• Currently, DDGS is used almost entirely as an animal feed although other uses of have been sought.

Protein types in seed meals based on their percentage of crude protein

Protien Type	Extraction Solvent	DDGS [43]	SBM [47]
Albumin	Water	2	--
Globulin	0.5 M NaCl	8	80
Prolamin	70% ETOH	50	--
Glutelin	0.1 M NaOH	17	--
Other	Unextracted	24	20

Very little is actually known as to how these plant proteins manifest adhesive properties although models have been proposed. Seed proteins exist in quaternary structures which have little or no adhesive properties. Seed proteins are characterized as globular structures with a hydrophobic interior. Denaturation of these proteins causes them to unfold into tertiary and secondary structures allowing them to express interior amino acids. In this study, seed proteins subjected to high temperature and pressure were able denature and express adhesive properties. As the proteins denature or unfold the hydrophilic and hydrophobic groups of the amino acids interact with wood carbohydrate portion through hydrogen bonding, Van der Waal forces and cross linking to create adhesion.

Adhesive strength is attributed to opening the coiled structure of proteins to allow for greater intermolecular interactions (Frihart & Lorenz, 2013). Heat and Pressure provides the means to uncoil proteins and allow for binding to occur with wood.



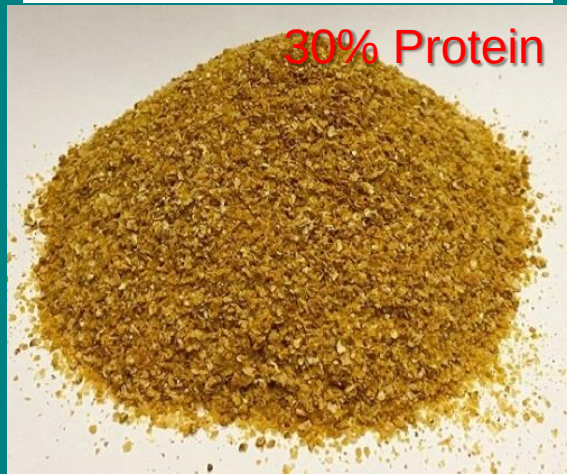
Amino Acid Composition of DDGS and Soya Flour Differ considerably

Amino Acid	Functional Group Characteristics	DDGS	SBM
Nonpolar:			
Alanine	hydrophobic	7.4	4.4
Isoleucine	hydrophobic	4.3	4.8
Leucine	hydrophobic	12.8	7.8
Methionine	hydrophobic	2.3	1.3
Phenylalanine	hydrophobic	5.5	5
Proline	hydrophobic	7.8	5
Trytophan	hydrophobic	0.8	1
Tyrosine	hydrophobic	4.7	3.6
Valine	hydrophobic	5.8	5.1
Total:		**51.4**	**37.9**
Polar:			
Arginine	positive charged/basic	5.5	7.3
Histidine	positive charged/basic	3.1	2.7
Lysine	positive charged/basic	3.9	6.6
Aspartic acid	negative charged/acidic	6.6	11.4
Glutamic acid	negative charged/acidic	12.8	17.2
Serine	uncharged	4.7	4.5
Threonine	uncharged	4.3	3.8
Total:		**40.9**	**53.5**
Other:			
Cystine	thiol	2	1.6
Glycine	hydrogen	4.3	4.3
Taurine	sulfonic acid	--	0.2
Hydroxy lysine		--	--
Hydroxyproline		0.4	--
Lanthionine		--	--
Ornithine		0.4	--
Total		**7**	**6**

Development of DDGS/Soya Flour Blends

- Over the past years, we have developed several DDGS-wood/fiber biocomposite products.
- We have found that DDGS can be blended with Soya flour to provide a more effective and less expensive adhesive than using Soya flour only to produce engineered wood products with mechanical properties that satisfy the industry standards.
- In this study, the performance of DDGS/Soya flour blends with various wood reinforcements are examined.



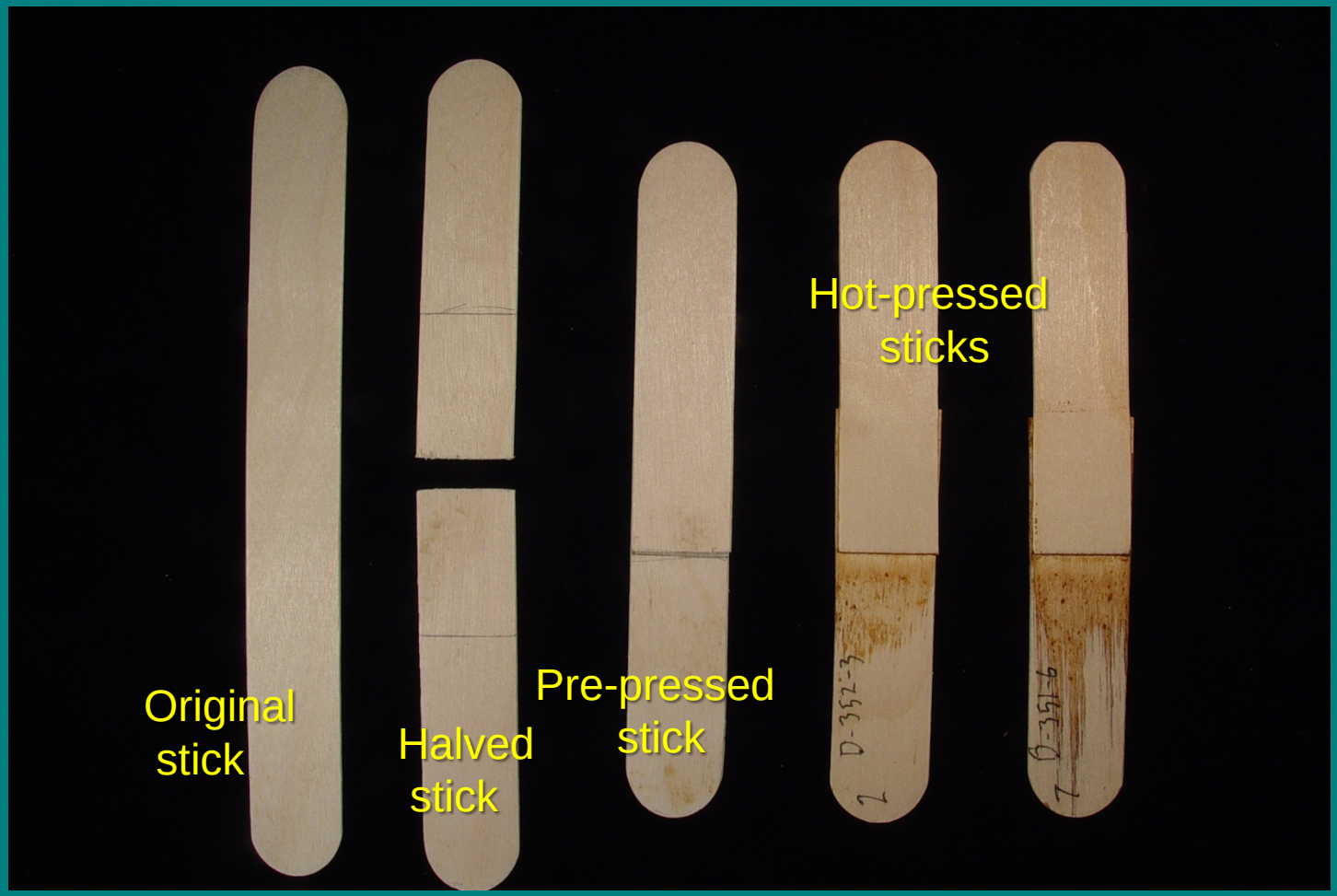


DDGS/Soya Flour formulations were tested with various wood reinforcement materials..

- Birch wood using birch popsicle sticks.
- Pine wood reinforcement to fabricated particleboard (PB)
- Paulownia wood reinforcement PB
- Red Mulberry wood reinforcement PB
- Eastern Red Cedar reinforcement PB

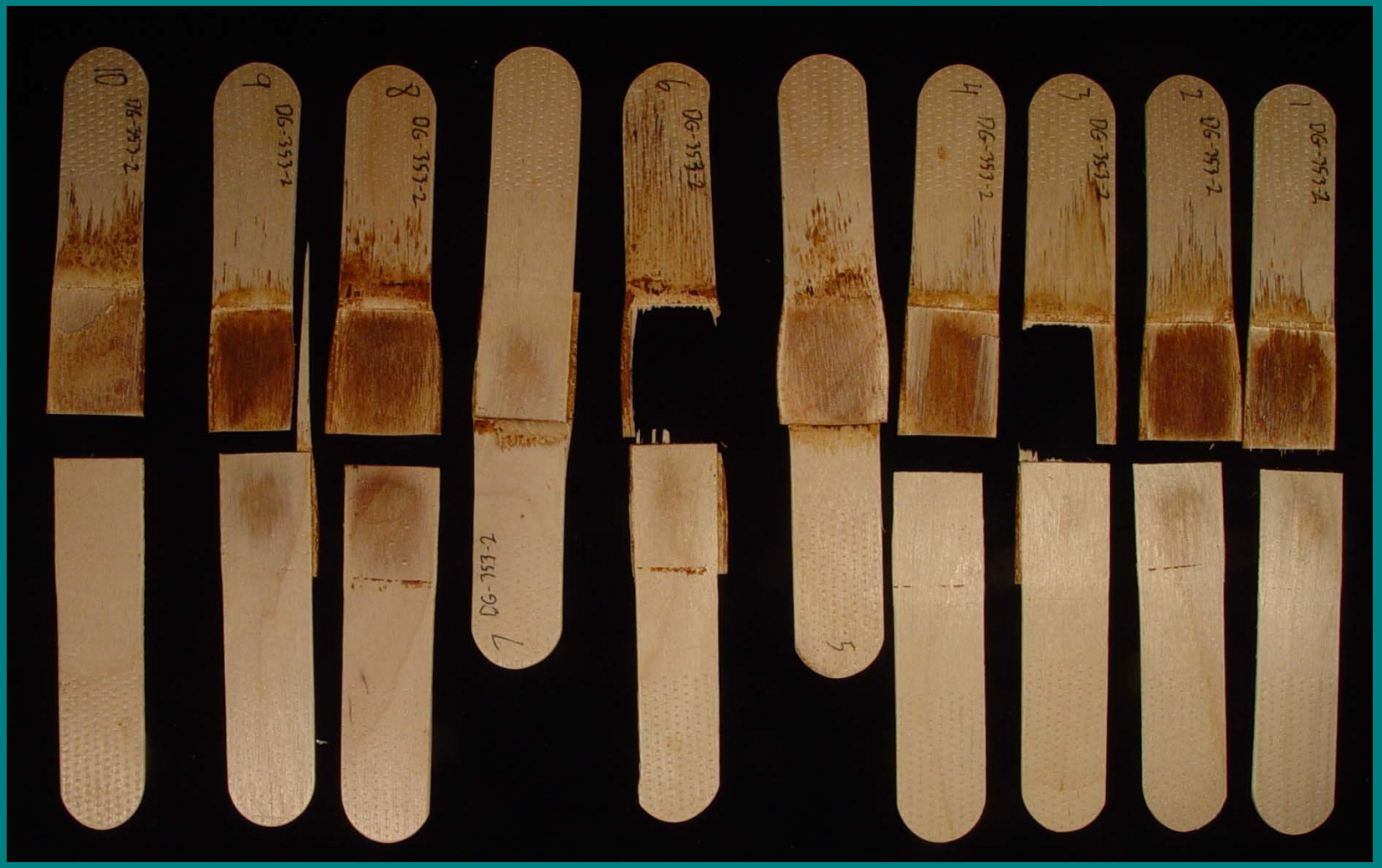


Adhesive properties (tensile or bonding strength) are determined by hot-pressing two White Birch popsicle sticks painted with DDGS/Soya flour slurry solutions.

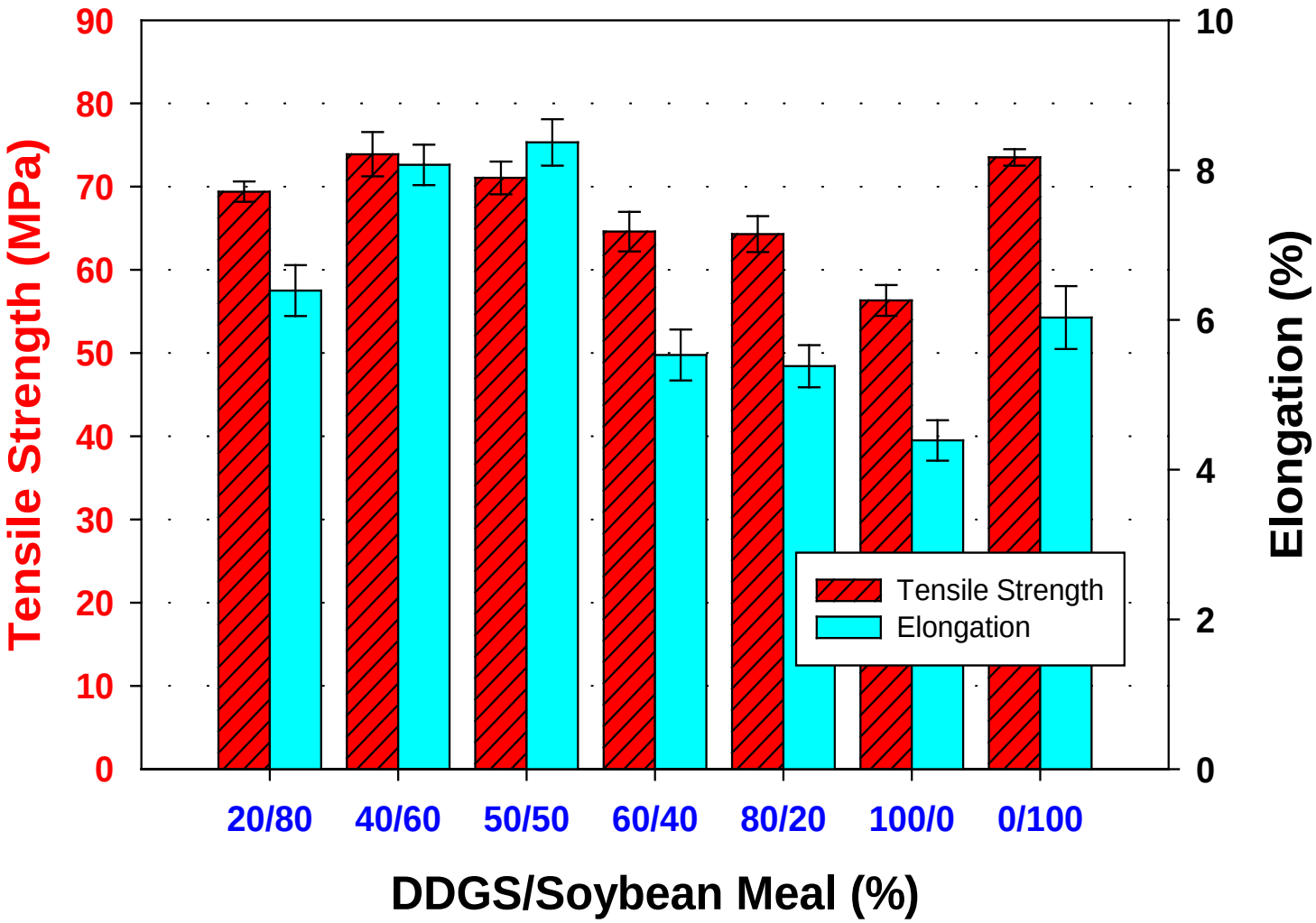


Mix 5 g flour:50 ml water for 30 min and apply 2 coatings. Press at 185 ^{o}C for 4 min under 8 Mton pressure

Examples of the strength of adhesive using a DDGS/Soya flour Formulation after Instron testing.



Adulteration of Defatted Soybean Meal with DDGS to Create an Effective Adhesive/Resin



Results of White Birch popsicle Stick Study

- As shown in this study, DDGS/Soya flour matrix were effective adhesives at 20, 40 and 50% DDGS blends with Soybean flour.
- Therefore, we employed a 50:50 blend in our later particleboard studies.



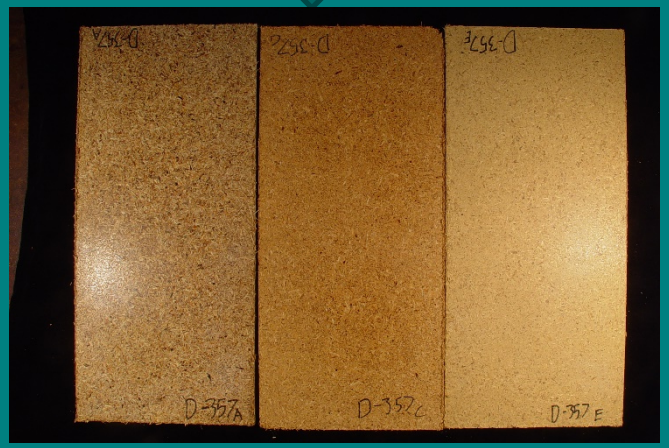




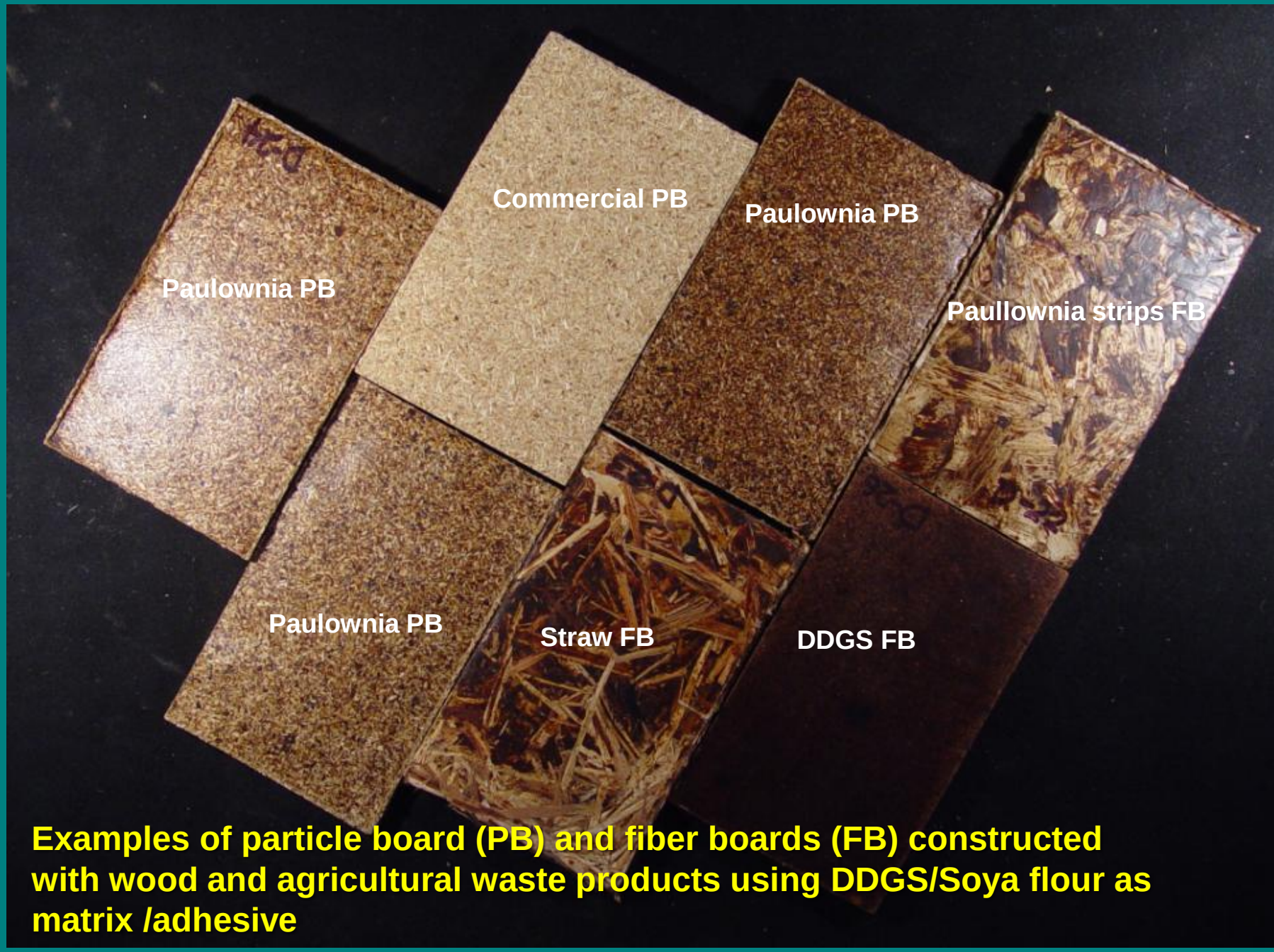
50% DDGS:50% Soya Flour

50% PW (#40):50% PW (#12-30)

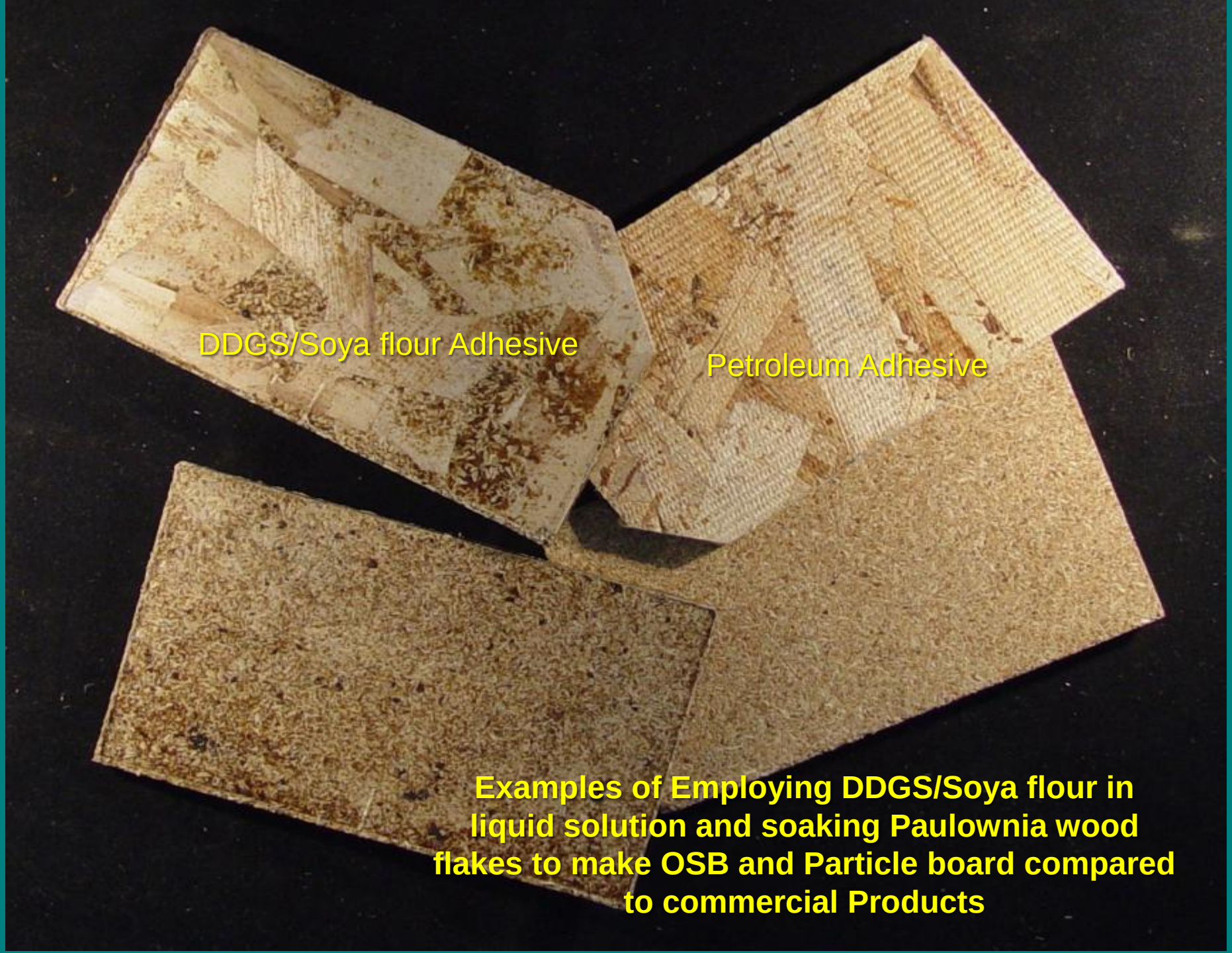
Preparation of bio-composite panels



Processing conditions:
Temperature: 185 °C,
Pressure: 5.6 MPa
Duration: 12 min
Carver Press



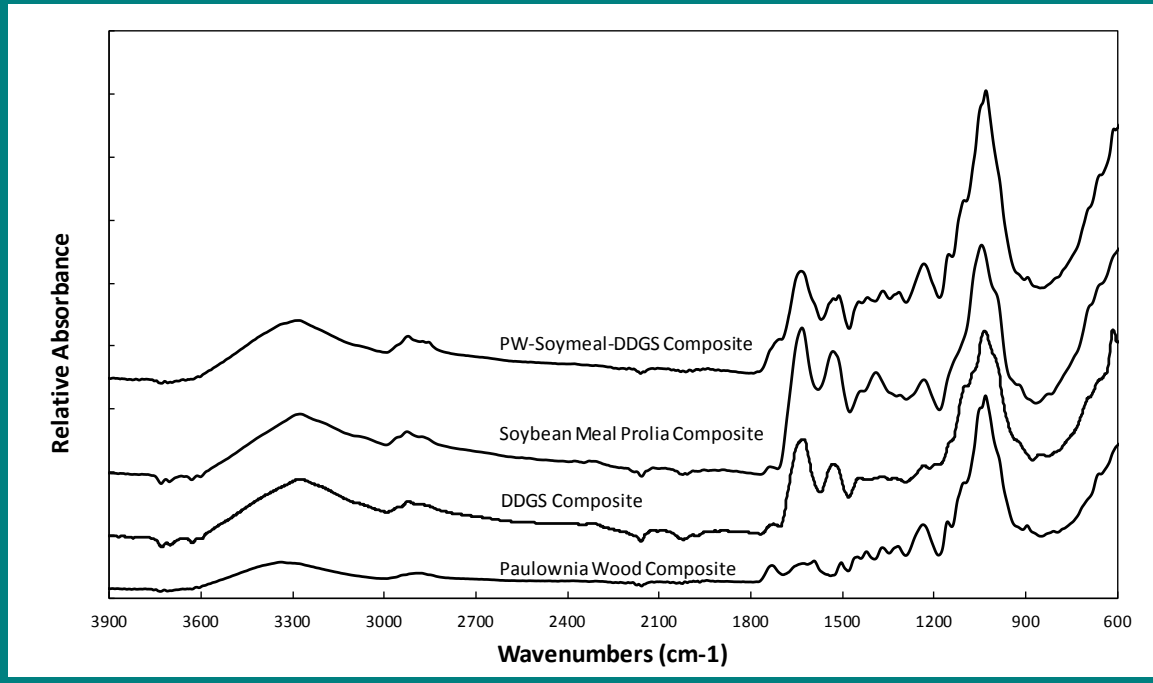
Examples of particle board (PB) and fiber boards (FB) constructed with wood and agricultural waste products using DDGS/Soya flour as matrix /adhesive

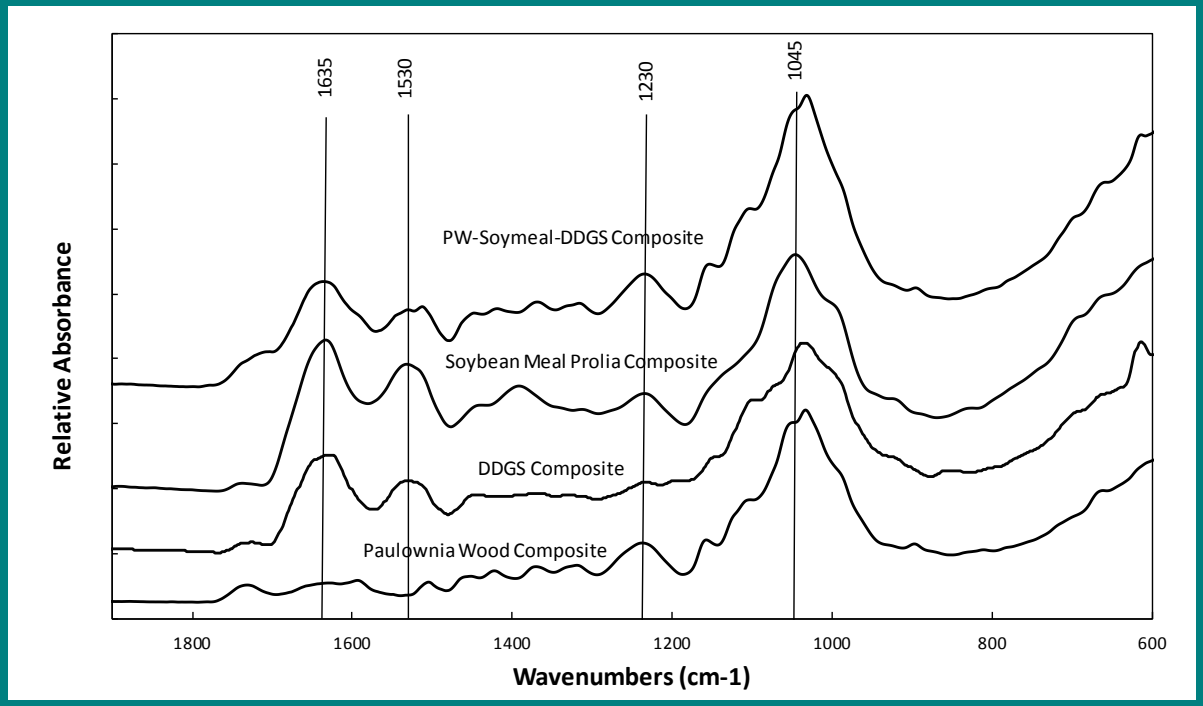


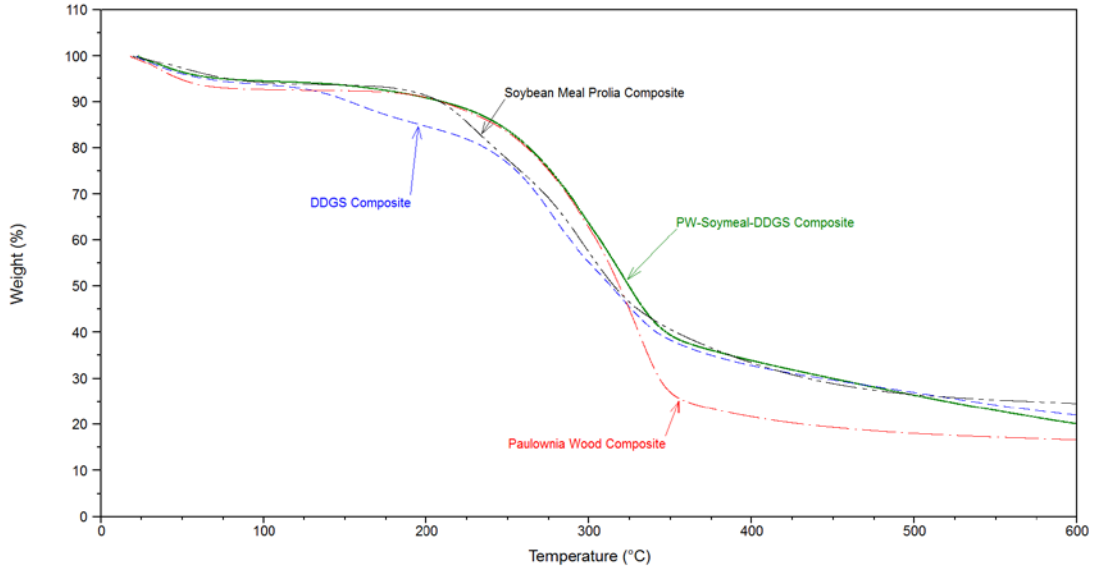
Examples of Employing DDGS/Soya flour in liquid solution and soaking Paulownia wood flakes to make OSB and Particle board compared to commercial Products

FTIR SPECTRA

PAULOUNIA WOOD COMPOSITE, PAULLONIA WOOD, SOYA MEAL, and DDGS

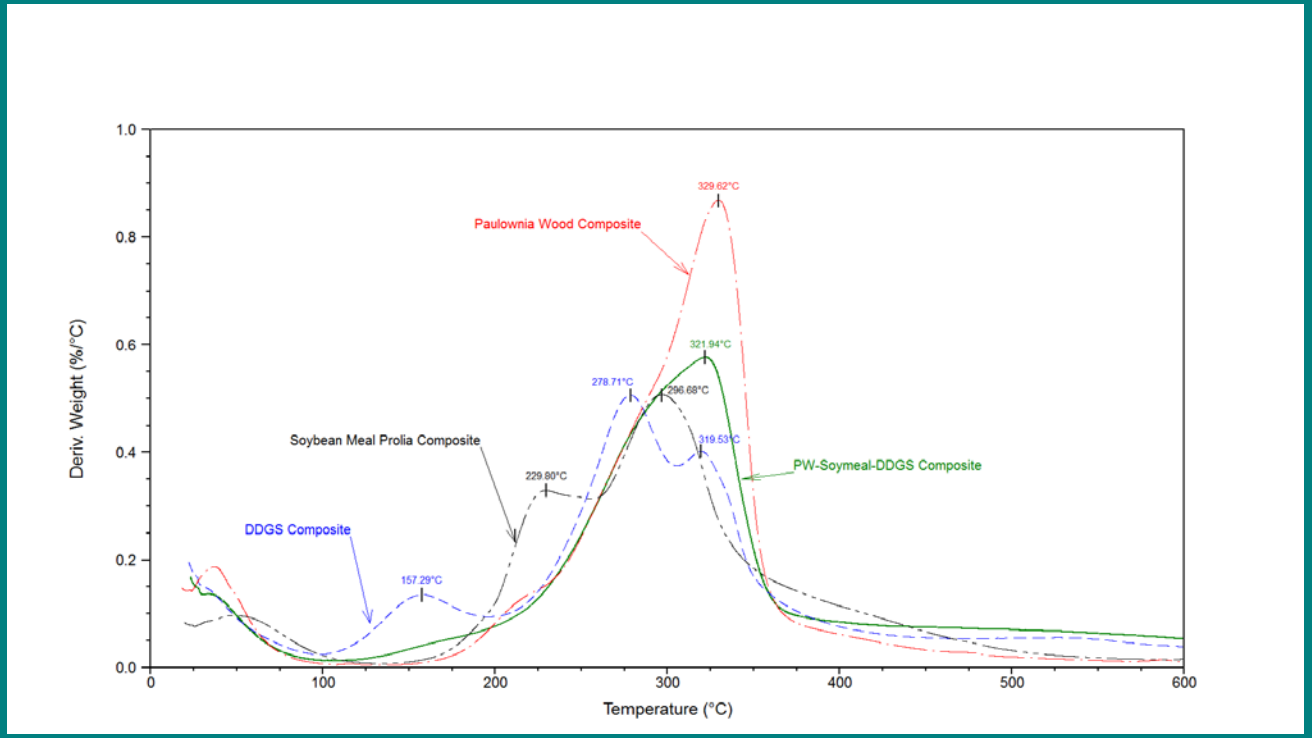






TGA- THERMOGRAMS

PAULOUNIA WOOD COMPOSITE, PAULLONIA WOOD, SOYA MEAL, and DDGS



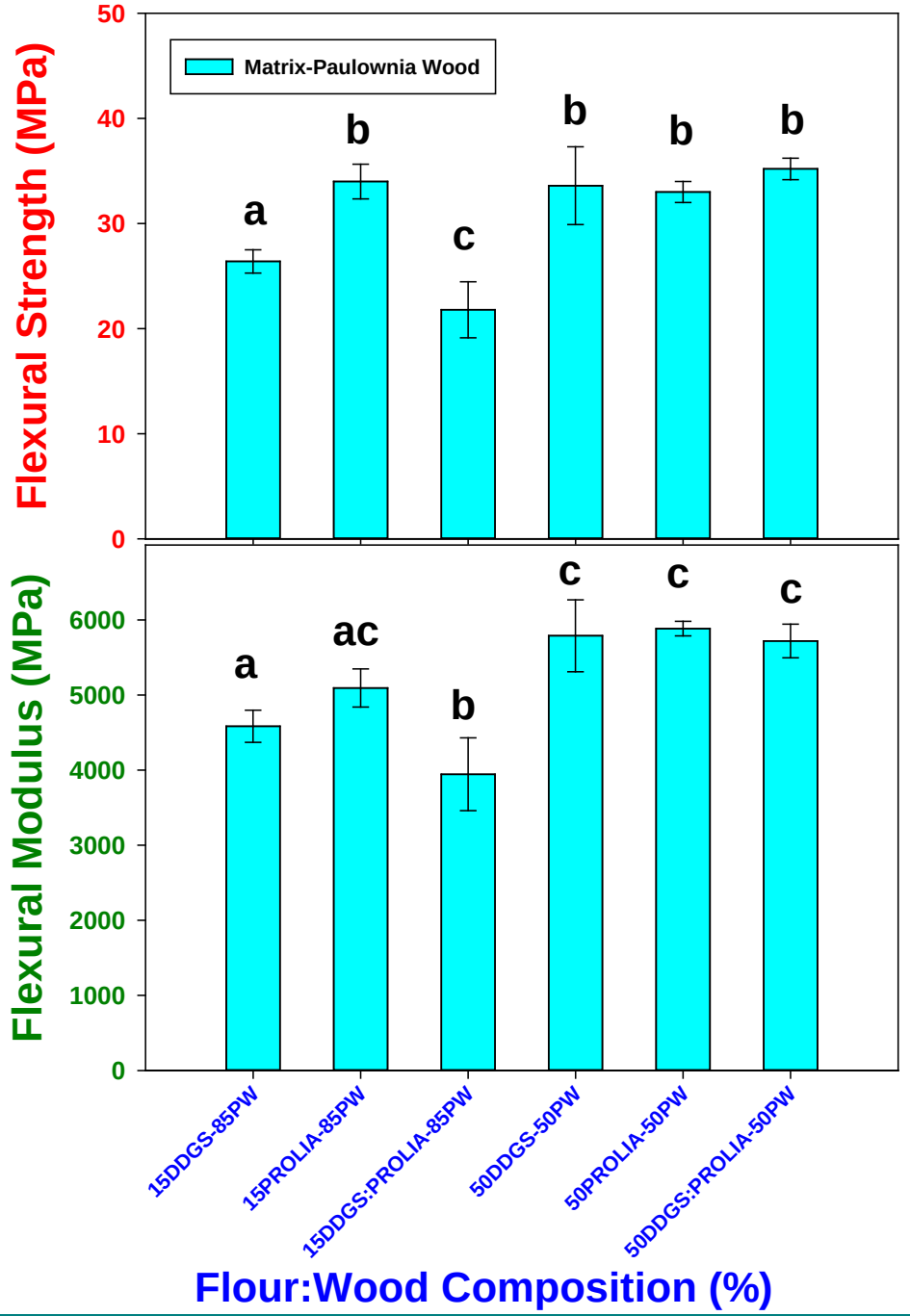
European Union (EN 312:2003) Standards for Particleboards and Commercial Medium and High Density fiberboard

Particleboard Specifications (Description, thickness)	Flex Strength (N/mm^2)	Flex Modulus (N/mm^2)
General Purpose PB/dry conditions, 3 to 6 mm	14	--
Interior PB (furniture grade)/dry conditions, 3 to 4 mm	13	1800
Non-load-bearing boards/humid conditions, 3 to 4 mm	13	1800
Load-bearing boards/dry conditions, 3 to 4 mm	15	1950
Load-bearing boards/Humid conditions, 3 to 4 mm	20	2550
Medium density fiberboard, MDF, 3 to 25.4 mm	24	2400
High density fiberboard, HDF, >5.5 mm	40	4000
10:90 SBM-DDGS-PW (%) composite panel, 4 mm	16	3500
15:85 SBM-DDGS-PW (%) composite panel, 4 mm	21	3900
25:75 SBM-DDGS-PW (%) composite panel, 4 mm	33	5550
50:50 SBM-DDGS-PW (%) composite panel, 3.5 mm	34	5700
75:25 SBM-DDGS-PW (%) composite panel, 3.5 mm	28	5200

Wood reinforcement employed is Paulownia Wood (PW)

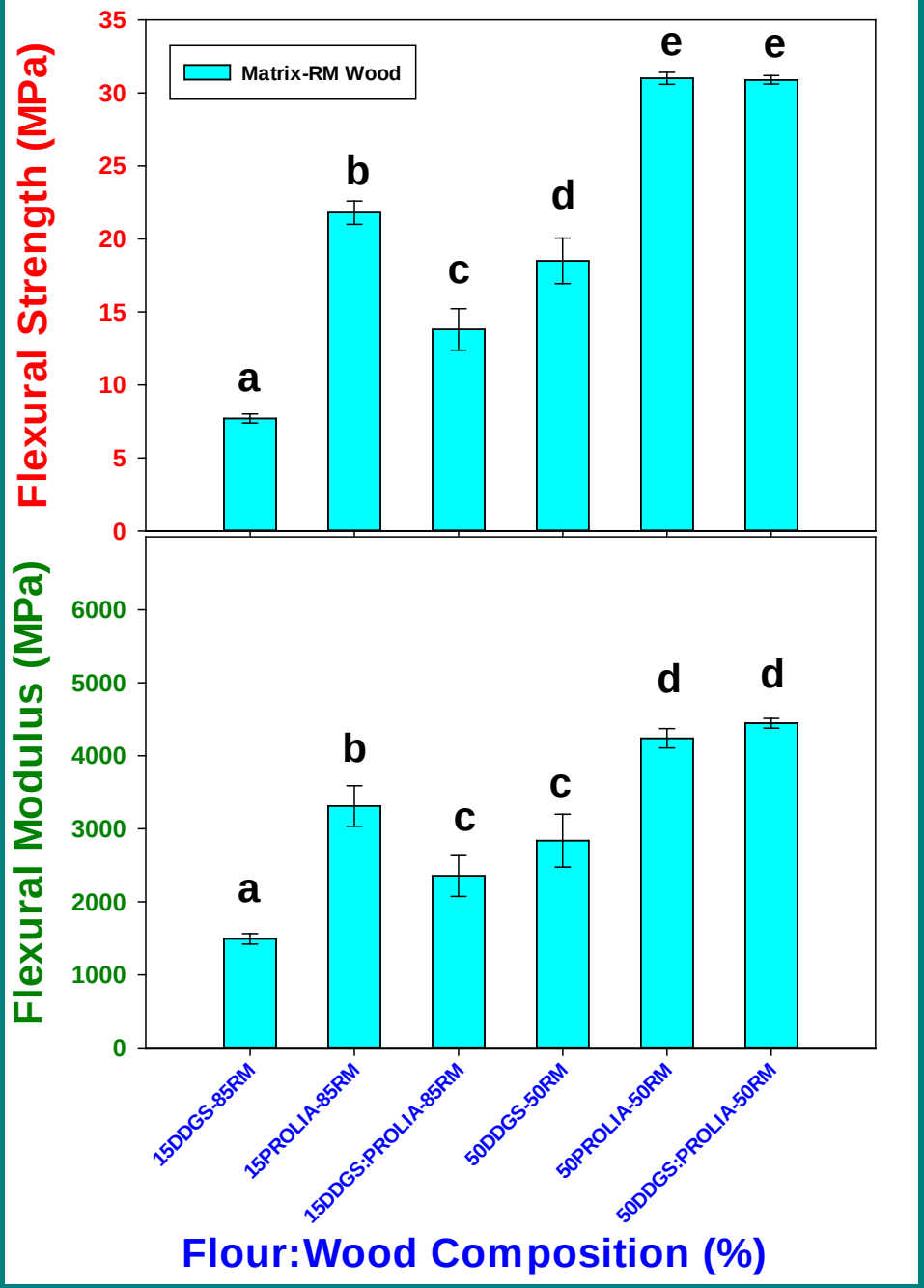
Influence of mixing DDGS and Soybean meal to create a Matrix using Paulownia as the reinforcement

- Oddly, the 15% matrix concentration using this wood did not response well to the DDGS: Prolia blend compared to the DDGS or Prolia matrix.
- No difference occurred for the 50% blend.



Influence of mixing DDGS and Soybean meal to create a Matrix using Red Mulberry wood as reinforcement

- As shown here, the 15% matrix concentration using DDGS:Prolia was not as effect as the Prolia only. These results differ from pine wood.
- The 50% Prolia and 50% DDGS:Prolia blends exhibit the same mechanical properties.



Wood Source was critical for good results using the 15% matrix: 85% wood Formulations.

- Birch, Pine and Eastern Red Cedar wood respond well to a 50:50 blend of DDGS:Soya Flour, exhibiting mechanical properties that were close to 100% soya flour matrix.
- When the Paulownia and Red mulberry wood was used, lower mechanical were obtained from the panels.

Conclusions

- Novel DDGS/Soya flour-wood composites were fabricated. We suspect that protein content alone is not completely responsible for the entire adhesive nature of DDGS.
- Little difference in mechanical properties were obtain using a 50%matrix:50% wood blends regardless of the wood type employed.
- Considerable difference in mechanical properties were obtained with a 15% matrix:85% wood formulation depending on the wood type employed.
- Regardless, DDGS/Soya flour-wood composite panels were found to be comparable or superior to mechanical properties required by Industry standards (EN 312:2003).

Future Directions

- Develop improved methods to process DDGS to be blended with Soya flour to create a usable adhesive.
- Develop “improved DDGS/Soya flour adhesive formulations” to compete with petroleum-based adhesives. Partner with interested groups that can provide “useful DDGS/Soya flour” sources and formulations.
- Employ new avenues to commercialize DDGS/Soya Adhesive by its incorporation in flake board, wafer board and plywood. In addition, the DDGS/Soya flour adhesive could be employed in fiber/mat molding operations to make light-weight panels for automobiles.


Thank you!

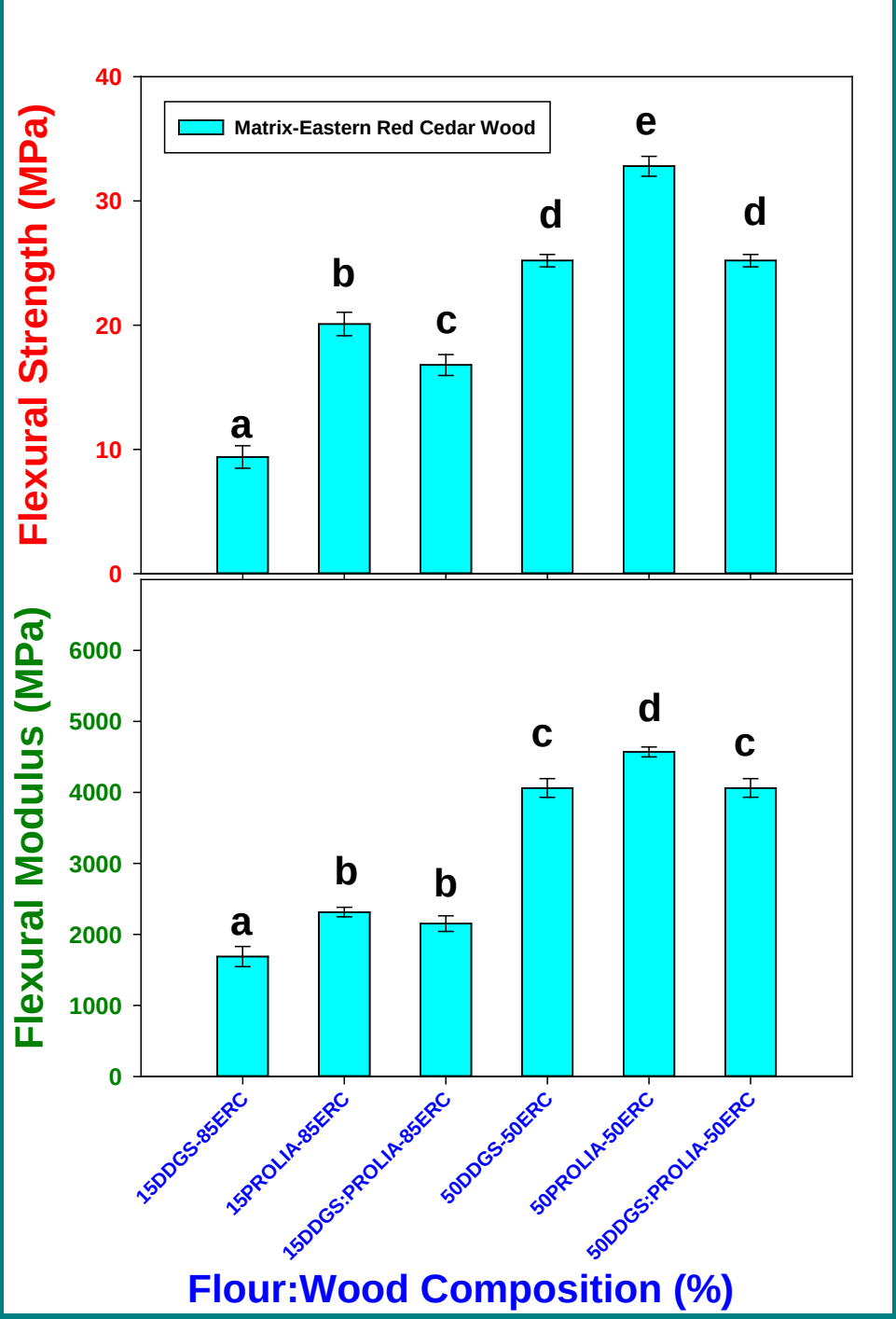
Additional Information

Potential Non-Dietary Uses of DDGSs

- In the past, we have studied the use of DDGSs as a filler to be blended with thermoplastic resin matrix to fabricate “wood plastic composites”. The plastic is the matrix and the DDGS is an inert low cost filler. The idea is to lower the cost of producing plastic composites.
- More recently, our attention has turned toward the employment of a “modified DDGS” as an adhesive matrix in its own right. The DDGS adhesives have been employed to construct various engineered wood products.

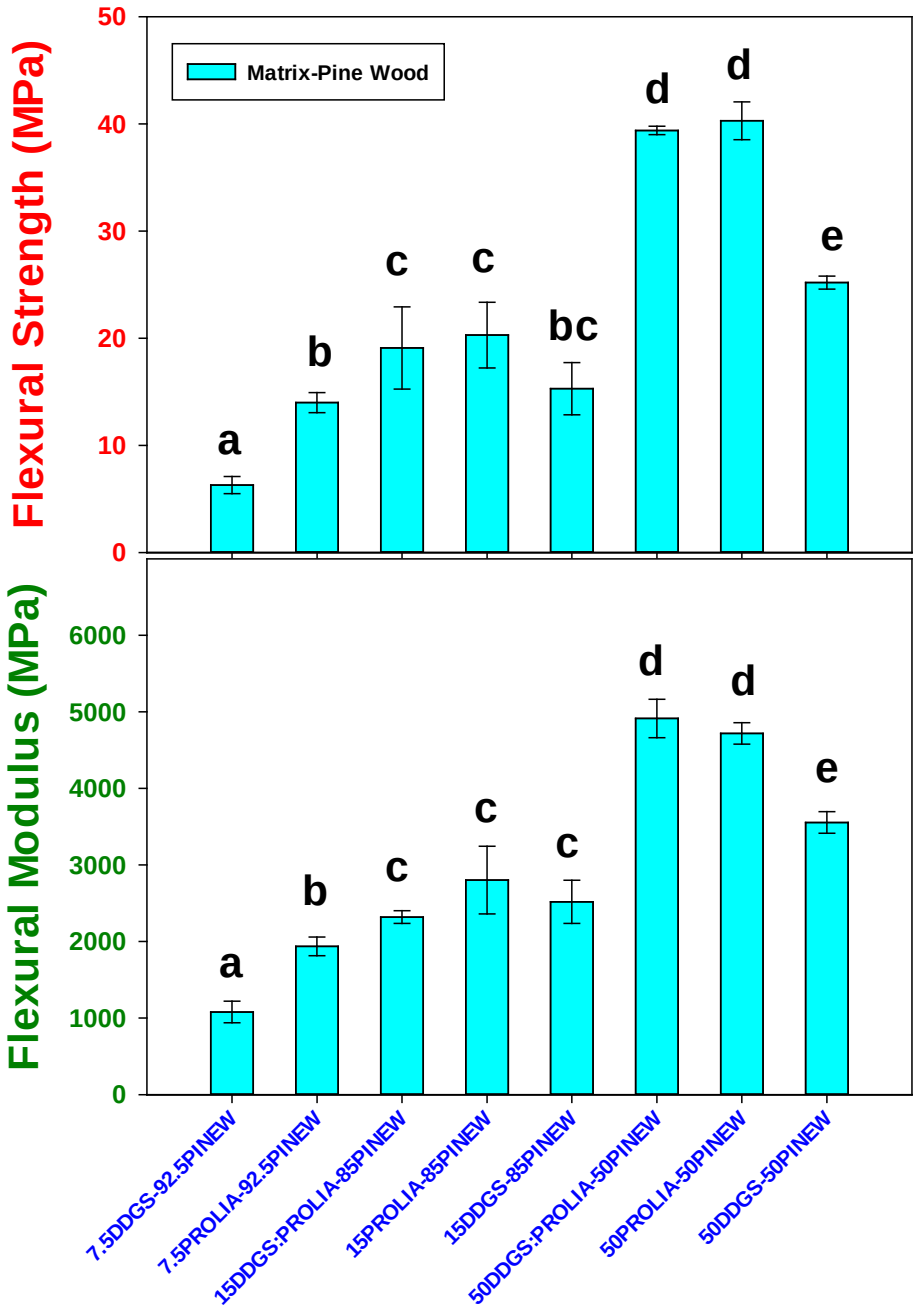
Influence of mixing DDGS and Soybean meal to create a Matrix using Eastern Red Cedar wood as reinforcement

- As shown here, the 15% matrix concentration using DDGS:Prolia was not as effect as the Prolia only. These results differ from pine wood.
- The 50% Prolia and 50% DDGS:Prolia blends exhibit the similar but slightly different mechanical properties.



Influence of mixing DDGS and Soybean meal to create a Matrix using Pine wood as reinforcement.

- This slide illustrates the effect of blending DDGS and Soya Flour (Prolia).
- As shown here increasing the concentration of the matrix greatly improves the mechanical properties.
- As shown, DDGS has an additive effect (borderline synergistic effect) when blended with Soya flour (Prolia) at a 15% matrix concentration.



International Agency for Research on Cancer

Centre International de Recherche sur le Cancer

IARC CLASSIFIES FORMALDEHYDE AS CARCINOGENIC TO HUMANS

- PRESS RELEASE N° 153/ June 15, 2004
- Formaldehyde is produced worldwide on a large scale. It is used mainly in the production of resins that are used as adhesives and binders for wood products, pulp, paper, glasswool and rockwool. Formaldehyde is also used extensively in the production of plastics and coatings, in textile finishing and in the manufacture of industrial chemicals. It is used as a disinfectant and preservative (formalin) in many applications.
- Engineered wood products are a major source of formaldehyde off-gassing in US homes and present a serious health problem. Formaldehyde is classified as a carcinogen, and its exposure levels are regulated in the USA to avoid health problems However, wood composite flooring made in China and exported to the US have formaldehyde emission levels that exceed current US safety emission standards, in some cases by as much as 350%.
-
- Sources: ClassAction.org. (2015). “Lumber liquidators class action lawsuit investigation over formaldehyde levels” & U.S. Consumer Product Safety Commission (CPSC) (2013). *An Update on Formaldehyde* (Publication 725. 2013 Revision 012013)