Soy-Based Additives for Enhanced Moisture Resistance in Wood Composites

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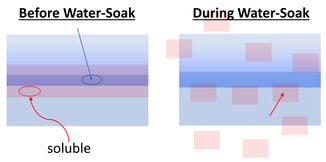
Introduction

Previous FTIR spectroscopy studies of failure interfaces have revealed that soy-based adhesives undergo partitioning during the wood lamination process, leading to a large proportion of water-soluble residue at the adhesive-wood interface, which produces a weak boundary layer with poor moisture resistance (Figure 1).[1]

Figure 1



The water-soluble fraction represents the "Achilles Heel" of current soy adhesive/binder systems.

NMR studies have revealed that these water-soluble components contain unreacted functional groups, including carbohydrate hydroxyls, carboxylic acids, and primary amines with exchanging protons.[2] In the present study, we have developed a methodology to screen co-reactants for their ability to react with water-soluble components, leading to a new type of soy meal additive that imparts improvements in the moisture resistance of wood composites. Demonstrations of relevant chemistry will be presented along with example applications.

We are developing surface treatments to mitigate the water-solubility of soy components, and to slow water ingress into wood composites.

One of our objectives is to develop facile chemistry that can be used to make moisture-resistant composites under conditions that typify most industrial processes.

Materials and Methods

Starting Materials:
- Ground Soy Meal, D50 = 45 µm;
- Rubinate-M PMDI (polymeric methylene diphenyl diisocyanate);
- Polymer Synergies ST-Compound (a proprietary reaction mixture).

Separation of Water-Soluble and Water-Insoluble Meal Extracts:
- Soak meal in water;
- Centrifuge and decant water-soluble components (first-cycle);
- Oven-dry water-soluble components at 40-50°C;
- Repeat washing/centrifuging for nine additional cycles, separate and dry the residual water-insoluble protein components.

Testing Reactivity with Water-Soluble Components:
- Reconstitute and dissolve water-soluble meal solids in DMSO;
- Separately, dissolve PMDI in DMSO;
- Mix the two reactant solutions (0.56/1 w/w meal/PMDI solids basis);
- Heat the mixed reactants for 2 hours at 80°C;
- Separately, heat the individual reactant solutions for 2 hours at 80°C;
- Analyze reactants and reaction products with SATR-FTIR.

Preparation of Surface-Treated Soy Meal Additive (STSM):
- Dry-blend Polymer Synergies ST compound with whole meal;
- Employ post-treatment heat cycle ~80°C.

STSM Analyses:
- Analyze starting reactants and STSM products with SATR-FTIR.

Preparation of Composites:
- 2-ply yellow poplar laminates, Soy-Flour/MgO adhesive[3] with and without 1% ST soy meal – Press 130°C, 4 minutes;
- PB composites (SYP), 3% PMDI, with and without 1% e-wax and 1% STSM – Press 200°C, 4 minutes;
- PP/maple wood composites (67/33 w/w), 175°C, Brabender roller-blade mixing, 16 minutes, with 1/3 w/w wax-SA[4], and with STSM/wax-SA blends, total additive level = 5% by weight.

Composite Evaluations:
- Water soak (PB and 2-ply composites);
- Contact Angle (PP/wood).

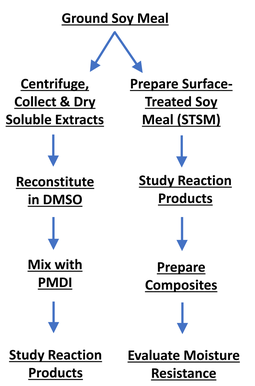
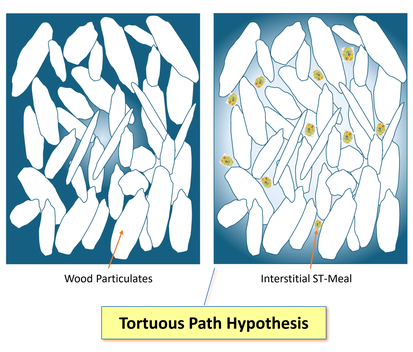


Figure 15: Schematic depicting interstitially dispersed ST-Meal and its possible effect on water ingress in wood composites



Results & Discussion

Reactions between PMDI and Water-Soluble Meal Components. After heating for 2 hours at 80°C, the individual PMDI and meal reactants remained stable in DMSO, whereas the mixture formed a compatible low-haze gel product, indicative of a homogeneous reaction. FTIR analyses of the reactants and products revealed the disappearance of free NCO from PMDI (Figure 3), as well as the disappearance of several bands from the water-soluble meal fraction, including a C-O stretch band, an -NH stretch band, and an -OH stretch band (Figures 3 and 4) to yield new types of absorption bands (Figure 5), consistent with urethane and urea linkages (Figure 7). Moreover, unlike the water-soluble meal reactants, the reaction products were observed to be insoluble in water (Figure 6). These results show that with the correct choice of co-reactants, water-soluble meal components can indeed be rendered as insoluble, suggesting that it should also be possible to chemically treat whole soy flour and/or whole soy meal powders to augment their moisture resistance.

Figure 2: Gelled Meal-PMDI Reaction Products

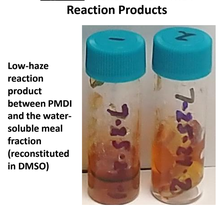


Figure 3: Solution FTIR of Reactants & Products

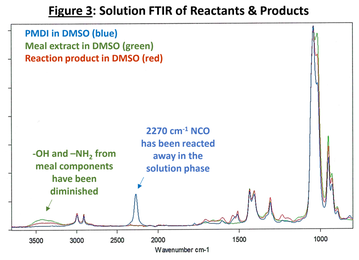


Figure 4: Solid State FTIR of Reactants & Products

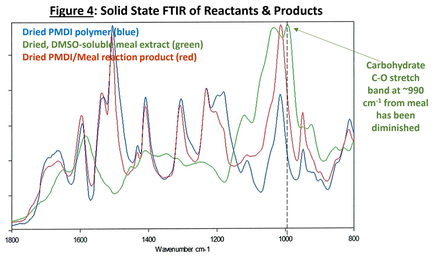


Figure 5: Solid State FTIR of Reactants & Subtraction Spectrum of Reaction Product MINUS PMDI aromatic null 1508 cm^{-1}, factor = 1.32

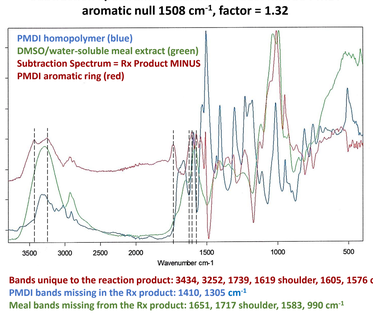


Figure 6: Solid reaction products reconstituted in water

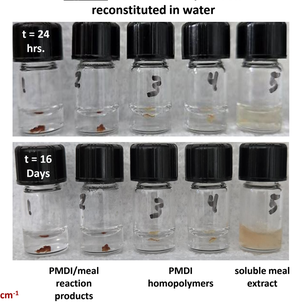
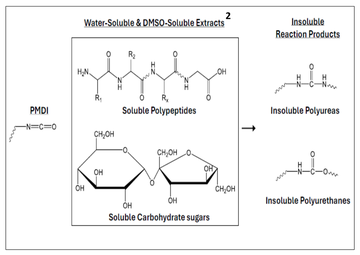


Figure 7: Reactants & Probable Reaction Products



Surface Treated Meal. The results of ST experiments have revealed that soy meal powder can indeed be rendered as hydrophobic via surface treatment with an appropriate combination of chemical reactants. Figure 8 illustrates surface treated whole meal powder floating on the surface of water. Aside from the chemical nature of the surface treatment itself, solid state FTIR studies have revealed that two types of mechanisms appear to be associated with the achievement of hydrophobicity. First, based on comparisons of neat and surface-treated versions of whole meal and water-insoluble fractions extracted therefrom, it appears that a portion of the soluble carbohydrates becomes physically encapsulated by the surface treatment, which likely inhibits diffusion (Figures 9 and 10). Second, it appears that a chemical reaction also occurs between select surface treatment components and indigenous components from the whole meal (Figure 11). In view of the PMDI reactivity results discussed above, it is likely that the reactive components from whole meal are the same water-soluble hydroxyl and amine containing moieties that were found to be reactive with neat PMDI.

Figure 8: Hydrophobic surface treated meal (left) vs. less hydrophobic meal powders

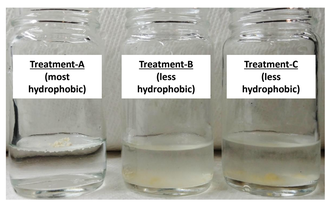


Figure 9: Solid state FTIR of non-treated and surface treated meal powders

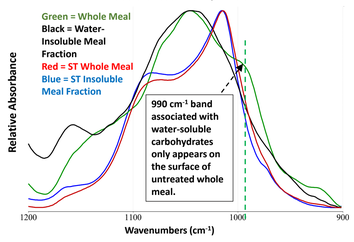


Figure 10: Subtraction spectrum ST whole meal MINUS ST insoluble fraction

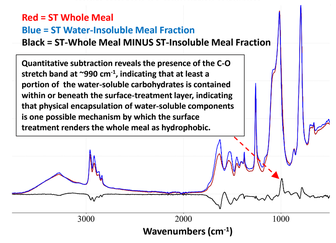


Figure 11: Solid State FTIR of Carbonyl Region

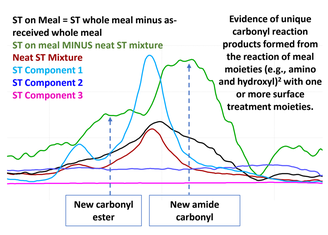


Figure 12: Receding water contact angle for PP/wood composites; t = 0 to 10 minutes; additive level = 5%

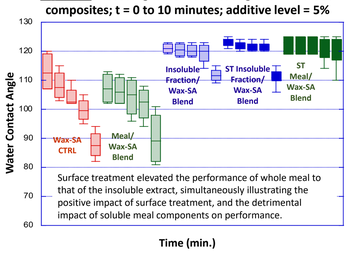
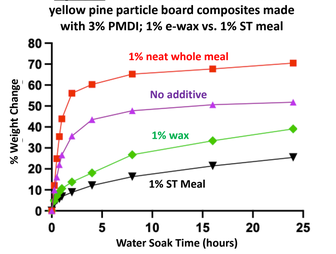


Figure 13: Moisture resistance of southern yellow pine particle board composites made with 3% PMDI; 1% e-wax vs. 1% ST meal



Moisture Resistant Wood Composites. As illustrated in Figure 12, PP/wood composites that contained insoluble-meal/wax-SA were more hydrophobic than those made with either wax-SA alone or with whole meal/wax-SA mixtures. This result is consistent with prior results which similarly showed that water-soluble components have a detrimental impact on the moisture resistance of composites.[1] By contrast, encapsulation with a surface treatment was observed to elevate the performance of whole meal to that of the water-insoluble extract, illustrating the positive effects of using a surface treatment to impart hydrophobicity and to mitigate the solubility of water-soluble components. Similarly, as shown in Figure 13, the moisture resistance of particle board made with 3% OD weight PMDI binder was significantly improved with the incorporation of 1% ST Meal in place of wax. Moreover, as shown in Figure 14, the moisture resistance of a soy flour/MgO plywood adhesive was also significantly improved with only 1% ST Meal substituted in place of an equivalent fraction of soy flour in the fully-formulated adhesive.

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Summary and Conclusions

As noted previously, the presence of unreacted water-soluble components in soy adhesives has been observed to negatively affect the moisture-resistance of wood composites.[1,2] For this reason, it remains important to identify reactive curatives that can undergo facile chemical reactions with these components; not only to yield moisture-resistant crosslinked networks, but to do so at rates that are commensurate with high-throughput production processes.

In this study, it has been shown that water-soluble components from soy meal can indeed undergo facile solution-phase chemical reactions with appropriately chosen electrophilic co-reactants (e.g., -NCO) to yield water-insoluble network-forming polymers. Moreover, when appropriate co-reactants are employed, it has also been shown that it is possible to produce hydrophobic meal particulates via heterogeneous dry-blend processes, where the surface treatment's reactive moieties appear to react with a portion of the water-soluble meal components while physically encapsulating the remainder.

The hydrophobicity of the treated powders appears to depend not only on the structure of the surface treatment, but also on the surface treatment's ability to immobilize the water-soluble components, which in turn suppresses their water solubility and helps to mitigate desorption of the surface-adsorbed components.

It has also been discovered that small levels of surface treated soy meal can be added to conventional binder and adhesive systems to yield wood composites with enhanced moisture resistance. Regarding the surprisingly low levels that are needed, it is plausible that a macroscopic version of a tortuous path mechanism[5] may be operative, where diffusion of water is inhibited by interstitially dispersed surface-treated particulates, that not only repel water, but also limit the number of contiguous pathways for moisture diffusion (Figure 15).

Future Research

We are continuing to employ FTIR and NMR imaging to test our mechanistic hypotheses and to help us in our efforts to create various types of surface treated meals and curatives for use in multiple applications, including soy-based binders for particle board; adhesives for plywood; hydrophobic additives for other composites; and UV-absorbing hydrophobic processing aids for polymer/wood composites.

Acknowledgements

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Figure 14: Moisture resistance of yellow poplar plywood laminates made with soy/MgO; with and without ST meal

Water Soak Cycle#	Soy/MgO Adhesive Control	1 % STSM Substitution for Soy Flour
Cycle-1	PASS	PASS
Cycle-2	PASS	PASS
Cycle-3	PASS	PASS
Cycle-4	PASS	PASS
Cycle-5	MARGINAL	PASS
Cycle-6	FAIL	PASS
Cycle-7		PASS
Cycle-8		PASS
Cycle-9		PASS
Cycle-10		PASS
Cycle-11		MARGINAL