Comparing Soy Flour Wood Adhesives to Purified Soy Protein Adhesives

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Abstract

While economics dictate that soy-based wood adhesives be made with soy flour, much of the recent literature on soy-based wood adhesives has involved using soy protein isolate. The obvious assumption is that the additional carbohydrates in the flour but not in the isolate only serve as inert diluents. Our studies have shown that the isolate can provide 10 times the wet bond shear strength than the soy flour at near neutral pH. Various models to explain the difference in wood adhesive performance between soy flour and purified soy products were examined. Prior studies eliminated some hypotheses by showing that using different soy flours or adding chaotropic agents (urea, guanidine hydrochloride, or dicyandiamide) or surfactants (sodium dodecyl sulfate or cetyltrimethylammoniumbromide) did not improve wet bond strength. In this study, adding a variety of carbohydrates to commercial soy protein isolate caused some drop in wet bond strength, but the carbohydrate plus commercial isolate is still much better than soy flour or a commercial soy concentrate. This cast doubts on the carbohydrate interference model, and left still unexplained why the commercial isolate is so much better than other soy products.

Introduction

Proteins have long been used in nature and by man as adhesives; in fact, they were the dominant adhesives for wood bonding for a long time (Lambuth 2003). Fossil fuel adhesives gained dominance since the mid-20th century due to ease of use, better moisture resistance, and lower cost. While the chemistry of these adhesives is well understood, the same is not true for protein adhesives. With the reemergence of soy adhesives, a better understanding of the structure-property relationship of soy products would be valuable for improving adhesives.

Although most proteins are made from the same approximately 20 amino acids, the ratios of amino acids and the sequence is unique for each protein. One question is whether there are some unique aspects of the proteins that may provide very good adhesive performance characteristics. Certainly, this is true for mussel protein adhesives that are known for forming good bonds even in aqueous environments. In this case, these adhesives contain dopamine, which in the presence of oxygen can form a quinone structure that will couple and cross-link the protein chains (Silverman and Roberto 2007). However, this chemistry is not of general utility in that dopamine or a ready precursor is not present in most proteins and would require the protein to remain in a low oxygen environment until the final curing step. Comparing the structure-property relationships for protein adhesives become difficult because the ones most commonly used for wood bonding (soy, casein and blood) are composed of many different proteins with widely different compositions and properties.

Soy flour is considered a good protein source for wood adhesives. It has a number of attributes including its wood bonding potential, low cost, abundant supply, and limited use in human foods. Original soy adhesives used flour under high pH conditions (pH > 10), because at a pH less than 10, soy flour does not possess the adhesive bond strength observed at the higher pHs (Lambuth 2003). More recent work on soy adhesives has concentrated on laboratory purified soy fractions including soy protein isolate (SPI) (Sun, 2005a). Commercial SPI has shown good dry and wet bond strength at neutral pHs (Frihart 2011). Unfortunately, the properties of the different soy products that are responsible for these observed performance differences have not been widely studied. There are abundant studies on the properties of the SPI and other purified soy proteins (Utsumi et al. 1997), and it was hoped that this information could be used to improve the performance of soy flour adhesives.

In considering the processes used to make defatted soy products, the first step for all products involves the crushing of the dehulled bean and fatty oil extraction. The resultant soy can be converted into a variety of products depending upon the end use. Without further purification, it can be ground into flour that is about 50 percent protein, with the remainder being nearly equal amounts of low molecular weight, soluble carbohydrates and higher molecular weight, insoluble carbohydrates. The soluble carbohydrates can be aqueous ethanol extracted to provide a residual protein concentrate (about 70 percent protein content), while removal of both soluble and insoluble carbohydrates provides the SPI (about –98 percent protein content). Studies using SPI could be related to flour performance if one assumes that the carbohydrates are just inert diluents. However, it might be possible that there are special effects of the carbohydrates and their interactions with the protein. The properties of many proteins are well covered in the food-related literature, as it is for soy proteins (Damodaran and Paraf 1997, Kinsella et al. 1985). However, the literature on the interaction of carbohydrates with proteins and soy flour is more limited (Tolstoguzov 1997).

Soy flour adhesives and casein adhesives were developed using high pH conditions with specific ratios of sodium and calcium hydroxides to promote dispersibility with the sodium hydroxide and final bond strength with the calcium hydroxide (Lambuth 2003). The use of high pHs probably allows the electrostatic repulsion of salt bridges to overcome the intra-molecular association of hydrophobic residues within the protein. Under these basic conditions, the soy also readily reacts with formaldehyde and other aldehydes. This has made it convenient for combining soy with phenolic resole resins either by blending or co-reaction (Lorenz et al. 2007).

The biggest recent change in soy adhesives has been the finding that soy flour can be co-reacted with polyamidoamine-epichlorohydrine (PAE) resins (Li 2007, Li et al. 2004). These products have found great utility in providing adhesives for interior wood products including decorative plywood, engineered wood flooring, and particleboard. One limitation of these reactions is that the PAE rapidly self-reacts at high pH conditions, which makes the products unstable and severely limits the ability of the PAE resin to react with the soy flour when used under caustic conditions. At neutral conditions, however, the PAE does an excellent job of improving wet strength of the soy flour adhesives, bringing them closer to the wet strength of the SPI.

This paper reviews former studies performed to understand the properties and increase the performance of soy flour using pH near neutral conditions. The experiments reported here

investigate whether soy flour can be imitated by physical mixtures of the various main components in soy flour, which are the protein and the soluble and insoluble carbohydrates. Different models to explain the performance will be presented and evaluated.

Materials and Methods

The soy protein isolate was PRO-FAM® 974 (ADM, Decatur, IL). Dextrin was from Cargill (Cedar Rapids, IA) and a-cellulose was obtained from Sigma-Aldrich (St. Louis, MO). The soy flour used as a comparison was Cargill Prolia™ 100/90 (Cedar Rapids, IA) and soy concentrate was Archer Daniels Midland Arcon F.

Soy isolate (15% of final concentration) was added to water containing the carbohydrate to be tested and mixed for 30 minutes. The amount of water used was adjusted to keep the same total weight; therefore, the amount of water was reduced as more carbohydrates were added. Soy isolate was compared to soy flour at 30% and soy concentrate at 20% in water, because at these concentrations, the amount of protein in the adhesive is approximately the same, at 15%.

An ABES (Automatic Bonding Evaluation System), Model 311c (Adhesive Evaluations Systems Inc., Corvallis, OR) was used for bonding and testing shear strength of the samples. Though the ABES does not have an associated standardized test method, it is useful for screening because it is rapid, relatively insensitive to rheological differences, produces uniform bonds on smooth veneer, and allows determination of the shear strength of bonds either dry or wet after soaking in water. Soy adhesive was applied to 5 mm on the end of one piece of maple veneer (1 17 mm × 20 mm × 0.6 mm thick), which was overlapped 5 mm with another piece of veneer. The sample was hot pressed in the ABES at 0.2 MPa for 120 seconds at 120°C. The bonded wood samples were equilibrated at 21 °C and 50 percent relative humidity at least 18 hours before testing dry or wet after soaking in water for 4 hours at room temperature. Five specimens were tested in tensile shear mode for each condition and the average and the standard deviation are shown.

Results and Discussion

Soy Performance Potential

The properties for the soy isolate (purified soy protein) should establish the best adhesive performance that can be expected for soy flour as a basic raw material source. Although SPIs are too expensive for commercial wood adhesive applications, they provide value for processed foods. Commercial SPIs are readily available; and thus, can be compared to soy flour as wood adhesives. ABES tensile shear tests showed that commercial SPI has about 10 times better strength with more wood failure after water exposure than the soy flour (Frihart 2011). Although the SPI was only slightly better than the flour under dry conditions at near neutral pH, the large reduction in shear strength for the flour adhesive after water exposure makes it unsuitable by itself as a wood adhesive. In studying the commercial SPI performance as an adhesive, the inherent assumption is that the carbohydrates in the flour are just inert diluents. Simply removing most of the soluble carbohydrates by aqueous ethanol extraction to make soy protein concentrate is not enough to give improved wet strength, adding support to the concept that the carbohydrates are inert diluents. However, the concentrate wet shear strength was much higher than the flour and closer to that of SPI with addition of a low level of the polyamidoamine-epichlorohydrin (PAE) coreactant than was that of soy flour (Frihart 2011). Thus, the PAE co-reactant can be a way to study the linking of proteins and protein-carbohydrates.

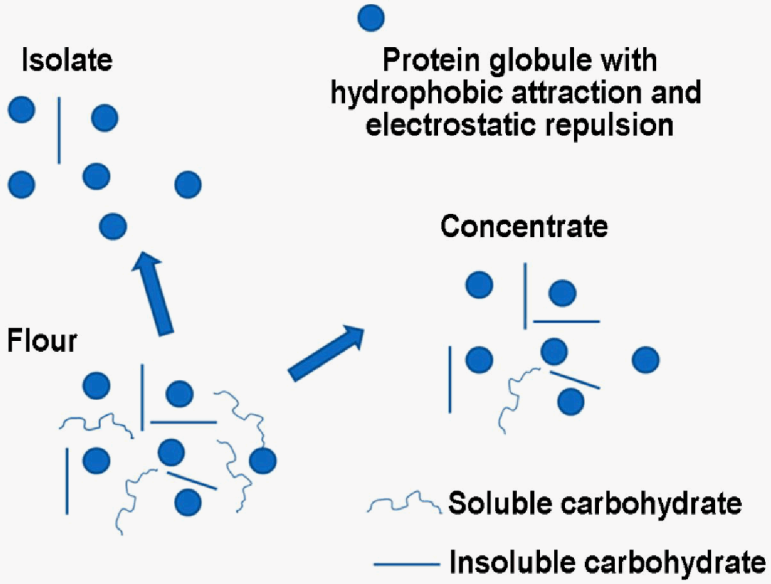

Figure 1. Carbohydrate physical interference model showing how the carbohydrates can limit protein agglomeration with the effect being greater for flour than concentrate.

This information supported the carbohydrate interference model, that is, the carbohydrates are not merely inert diluents, but may directly interfere with agglomeration of the proteins. Shown in Figure 1, this model involves spheres to represent the coiled protein structure, while the carbohydrates are represented by straight lines for the insoluble carbohydrates and squiggly lines for the soluble carbohydrates. Not surprisingly the isolated proteins should be free to agglomerate and provide the highest strength. Under dry conditions the proteins in the concentrate and flour can bond with the carbohydrates to give good performance, with soy flour having about 70% of the strength of the commercial isolate and a soy concentrate having about 85% of the bond strength. However, under wet conditions, the high affinity of the carbohydrates for water loosens these links and causes a large reduction in bond strength so that both the flour and concentrate strength were about 10% of the isolate. When a low level of PAE is present, the proteins can be linked by the PAE and bridge over the carbohydrates, changing the percentages to about 45% and 70% for the flour and a concentrate, respectively. This effect is more efficient with the concentrate because there are fewer carbohydrates to bridge over. The model in Figure 1 is consistent with this prior data (Frihart 2011), but this does not mean it is valid without further testing.

This model can be evaluated by adding carbohydrates to the SPI to see how much the bond strength drops off when tested under wet conditions. Our first experiments involved using dextrin for the soluble carbohydrate and cellulose for the insoluble carbohydrate. The dextrin was used since it is more likely to stay in the adhesive and affect bond strength than a lower molecular weight carbohydrate, such as sucrose that could easily migrate into the wood. The cellulose was used since it is a pure insoluble carbohydrate. The data in Figure 2 for the wet shear strength shows that although both the dextrin and cellulose cause a loss in strength at low addition levels, the effect levels out at 65% of the strength of the commercial isolate. The

addition of these carbohydrates separately or in combination does not cause an equivalent strength reduction to that observed with the flour and the concentrate at equivalent carbohydrate levels. Testing a variety of other carbohydrates (sucrose, galacturonic acid, pectin, and stractan) did not cause any great difference in results (not published). Thus, the data shows the carbohydrates can cause only a small effect, but are not the main explanation for why flour and concentrate are so much weaker in wet bonding than the commercial SPI.

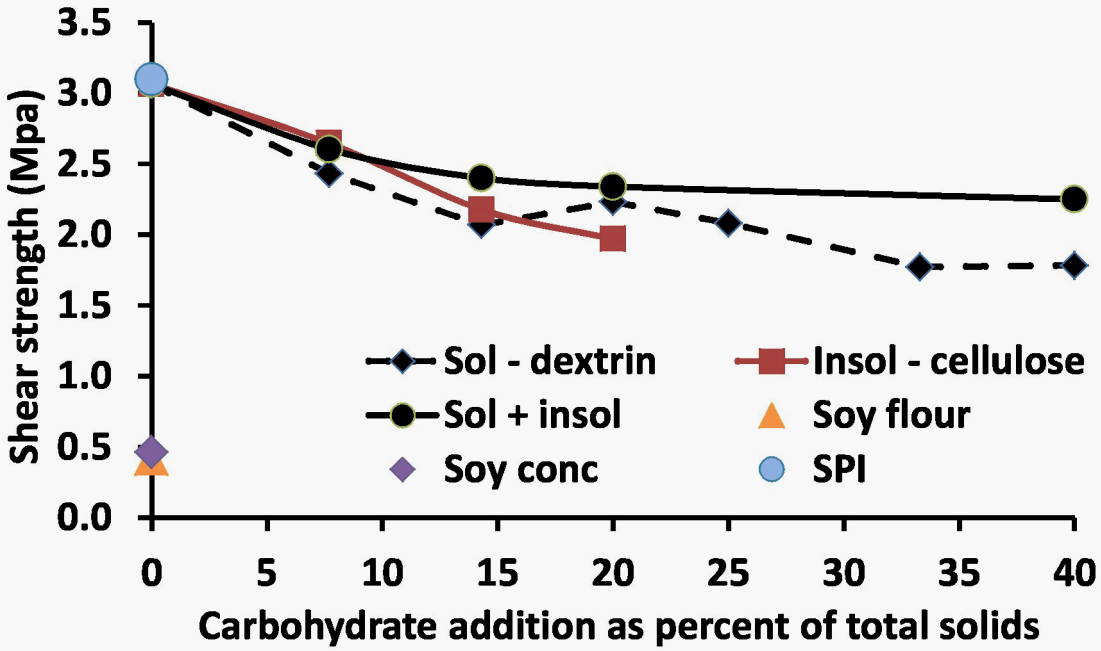

Figure 2. Effect on wet adhesive bond strength of addition of soluble and insoluble carbohydrates to SPI on wet adhesive shear bond strength. The total solids includes both the protein and carbohydrate added. For example, adhesive for the 40% data points contained 15g SPI and log of carbohydrate plus 75g of water.

Soy flour

Given that the carbohydrates do not explain the majority of the difference between the soy flour and the commercial SPI, we discuss here other models and factors that have been examined in the literature to try to understand this difference, Because soy flour gives such poor wet bond shear strength compared to the SPI, one question arose as to whether this was because of the type of soy flour that was used. Proteins exist either in their native state or denatured (non-native) state. There can be a whole variety of denatured states depending upon the conditions used to denature the protein. The flour with a high protein dispersibility index (PDI) is considered to be in its native state as it has been exposed to relatively little heat/chemical treatment that may cause denaturation. The commercial 90 PDI soy flour is prepared by using low processing temperatures and is highly dispersible. The other extreme is the commercial 20 PDI soy flour that uses higher processing temperatures, which denature many proteins and deactivate some, enzymes, such as urease. In between is the 70 PDI flour. It was expected that the 20 PDI should provide lower bond strengths due its poorer dispersibility, especially with larger particle size flour. Our data showed that neither of these assumptions is valid (Frihart and Satori 2013). Although the 20 PDI flour provides more viscous dispersions, the dry and wet strengths of the

bonded wood specimens without or with 5% PAE (s/s on soy) was independent of the PDI level of the soy. In addition, the shear strengths were virtually independent of particle size as well as the amount of soy flour dispersed in water. Thus, surprisingly the final bond strength was quite independent of the type of soy flour, even though many other properties of the flours were quite different.

Chemical Denaturation

Because of the low free energy differences between different conformations of a protein, many environmental factors have been shown to alter the protein properties (Pain 2000). Thus, it seemed logical that adding materials that alter the protein structure can expose more of the reactive amino acids for interacting with other proteins or with a possible PAE co-reactant. This concept was supported by published work showing adding chemical denaturants improved the wet bond strength of SPI (Sun 2005a).

The literature covers extensively the composition and structure of proteins, but for this paper it is important to understand only a few aspects. Although soy proteins have an abundance of potentially reactive functional groups (Sun 2005b), many of these are not available for reaction. Because of the proteins' hydrophobic nature, they coil and aggregate with other protein chains to minimize the interaction with water. Though some of the polar groups are on the surface, many more are buried inside the coiled protein globule and stabilized by hydrogen, salt, and other polar bonds. Given the compositional complexity of proteins in general and soy flour specifically, it is hard to determine what specific reactions are taking place between the soy proteins and carbohydrates and a PAE co-reactant. However, the properties of the cured product are not what would be expected of a highly cross-linked product in terms of stiffness when exposed to heat or solvents. Thus, another approach to improving the soy properties was to examine ways to open up the protein structure for better protein-protein and protein-PAE interactions.

One way proteins are altered is to add chaotropic agents like urea, guanidine hydrochloride, or dicyandiamide; they can function by swelling the protein structure either by being absorbed into the proteins or by altering the polarity of the aqueous matrix, as illustrated in Figure 3. The concept is that the chaotropic agent causes the protein to swell so that when the proteins aggregate it is not just a surface phenomenon, but an actual entanglement between the protein chains. Chaotropic agents have been shown to improve the strength properties of laboratory soy protein isolates (Sun 2005a); thus, it was expected to also be effective with soy flour. However, none of the chaotropic agents were effective in dramatically improving the dry or wet shear strength of 90 PDI soy flour adhesives (Frihart and Lorenz 2013).

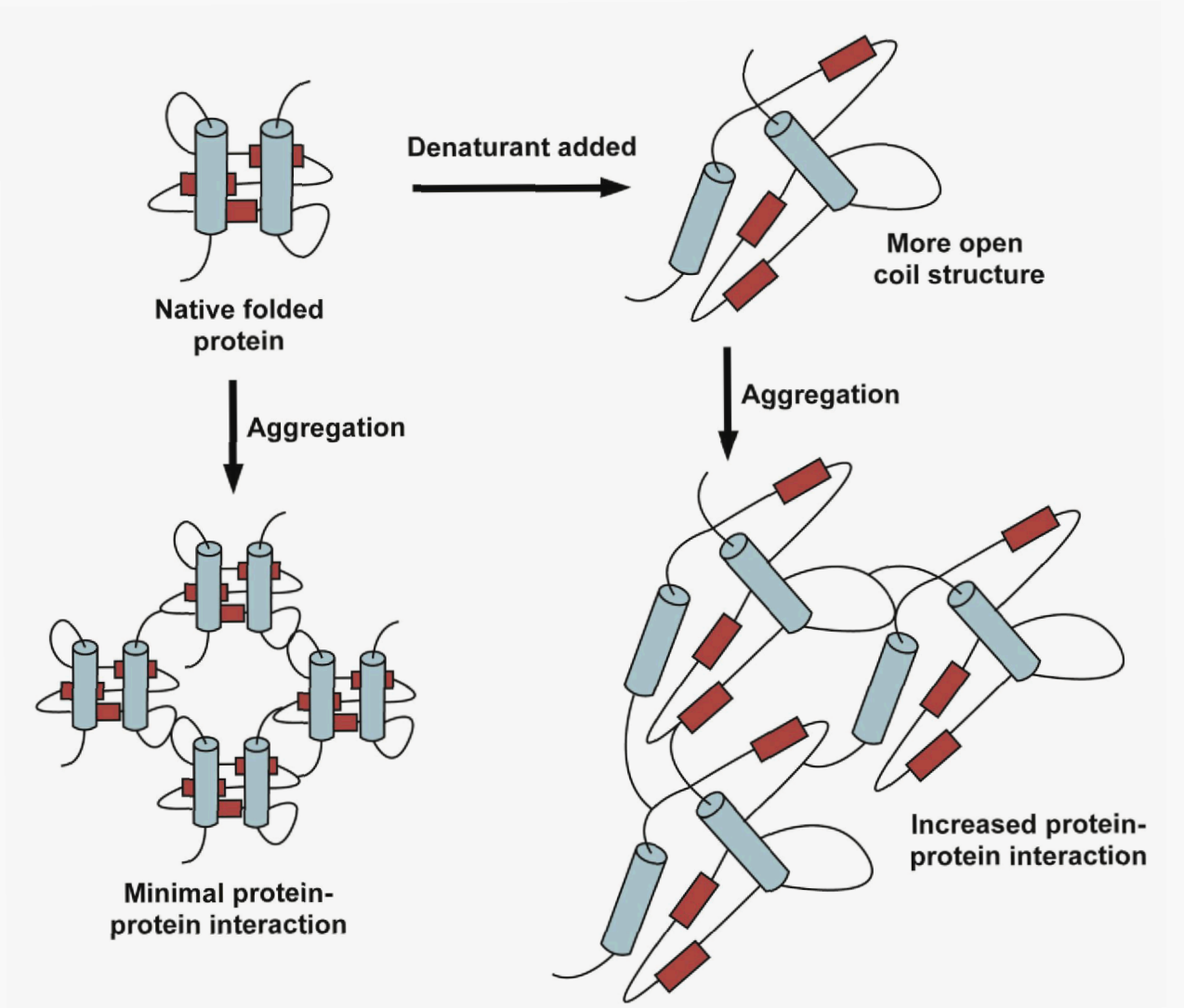

Figure 3. Uncoiling of the protein by adding a denaturant (chaotropic agent) can enhance protein-protein interaction (shown) and reaction with PAE co-curing agent (not shown).

Another way to potentially open up the soy protein structure is to add surfactants that can help solubilize the hydrophobic domains. Again, this route was demonstrated to be useful for improving the bond strength of SPI (Sun 2005a). Alas, the route was not effective with 90 PDI soy flour using sodium dodecylsulfate and cetyltrimethylammonium bromide surfactants, as well as a variety of other surfactants (Frihart and Lorenz 2013). Along the same lines, the use of water soluble co-solvents is another route to solubilize the hydrophobic domains to increase the access to the polar sites and increase the interactions beneficial for improved adhesive performance. The use of glycerine and 1,2-propanediolas less polar co-solvents did not help in making a more water resistant adhesive (Frihart and Lorenz 2013).

One concern is that adding these small molecules, such as chaotropic agents, surfactants or co-solvents, to make the soy proteins more suitable for forming stronger bonds, could be offset by the plasticizing effect of the small molecules. A rather unique feature of wood compared to other substrates is its ability to absorb small molecules effectively removing them from the bondline.

This has been demonstrated by the increased stiffness of soy adhesive in wood bonds than when absorbed onto an inert substrate like fiberglass (O'Dell et. al. 2013). Although the plasticization effect could still exist with wood as a substrate, it is less likely to be a major factor.

Conclusions

The studies on soy adhesives have yet to explain why soy flour adhesives provide nowhere near the same strength as the SPI adhesives, especially under wet conditions. Several hypotheses to explain this result have been examined, but none really explain this large difference. One thing that is clear is that commercial SPI with added soluble and insoluble carbohydrates caused the wet strength to drop to no less than 65% of its original value, but this is far short of the 10% of the SPI wet strength observed for the soy flour and a commercial concentrate. The added carbohydrates are playing a minor role as a physical interference for protein-protein interactions. The addition of selected chaotropic agents, surfactants or co-solvents to soy flour did not provide stronger adhesive bonds, while most of these chemicals improved the strength of SPI adhesives (Sun 2005a). Thus additional insight is needed to explain the difference between SPI and soy flour adhesives.

To be an effective adhesive, the soy concentration needs to be high, which leads to viscous solutions. This indicates strong interactions between soy particles and may explain the inability of the proteins in soy flour to rearrange to a more active state. This interference has been explained as macromolecular crowding and may explain why the protein in soy flour cannot be readily converted to a more active state.

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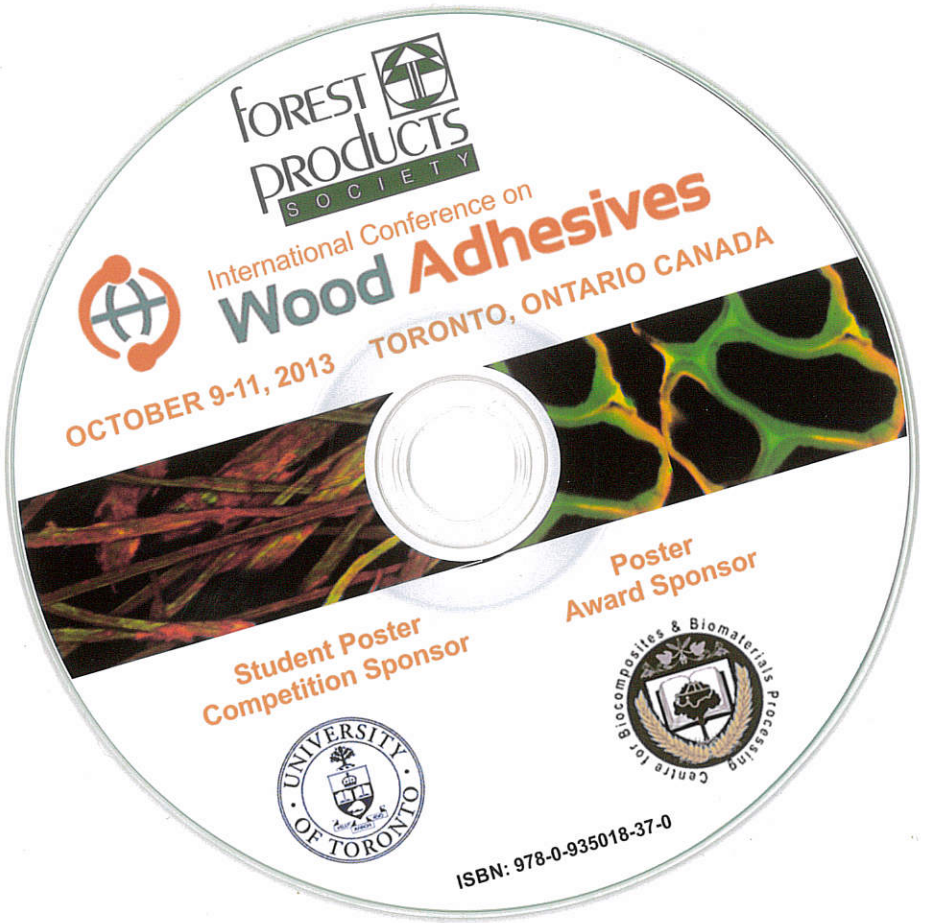
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