Sticking power from soya beans

Higher fossil fuel prices and concerns over formaldehyde in existing glue formulations have led to a resurgence in interest in soya-based adhesives, report James Wescott & Charles Frihart

Soya beans have long been considered a miracle crop for their ease of growing; high concentration of vegetable oil and high protein content; and their ability to reintroduce nitrogen back into the soil. The origin of soya beans dates back to the early 11th century from the eastern half of China. They were introduced to Europe in 1712 and first harvested in the US in 1764. With the advent of the combine harvester, soya bean growth exploded in the US from 1929 to 1939, increasing from 0.23m to 2.25m t.[1]

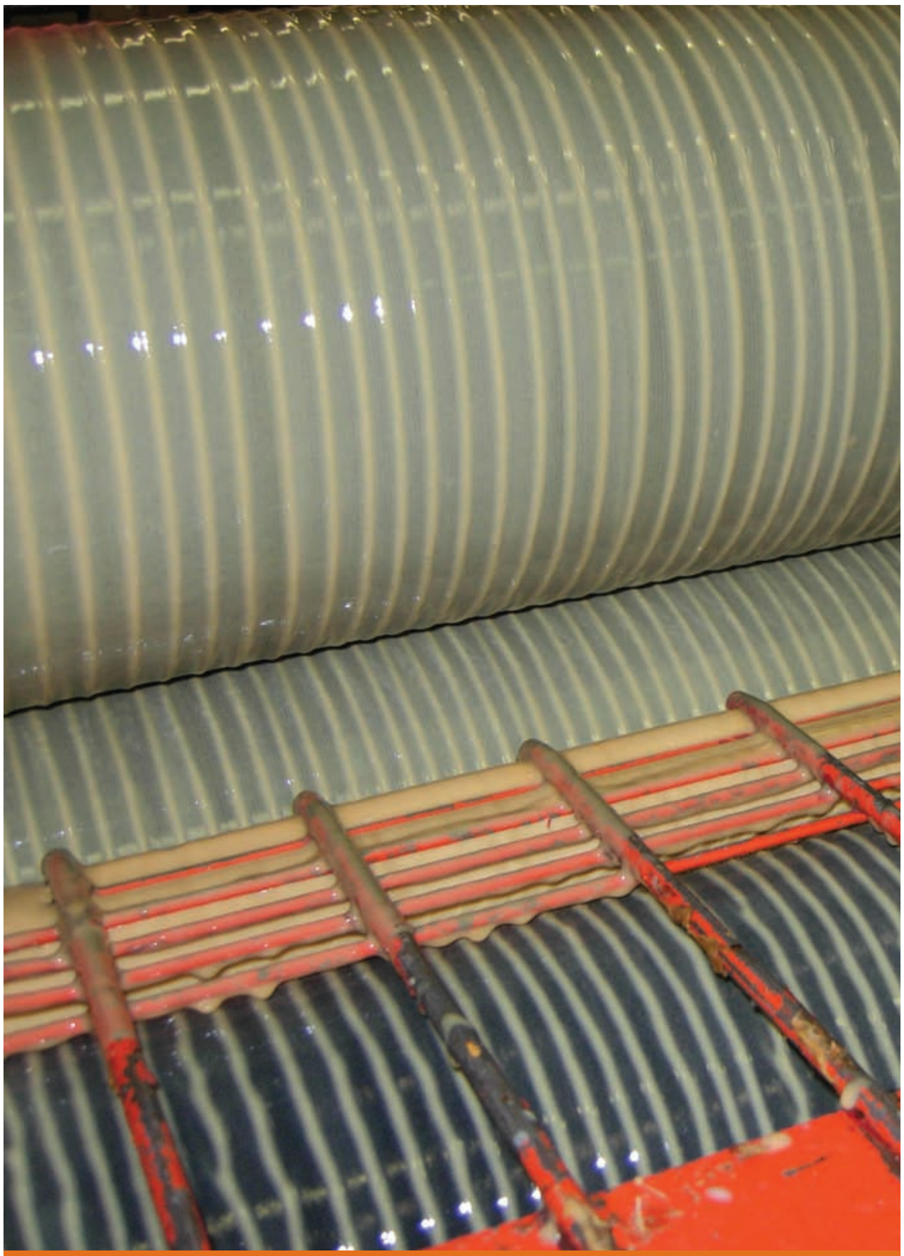
Today, soya beans are grown throughout the world. In 2008, an estimated 221m t of soya beans were produced.[2] The US led the way with 36% of the total harvest, followed by Brazil, Argentina, and China, with 25%, 20%, and 8%, respectively. For much of their history, soya beans were grown for their valuable vegetable oil; and the protein-rich meal was considered to be a secondary product. A much more recent development, however, is the production of soya-based adhesives, made by denaturing soya meal or flour.

Soya adhesives

The first US patent for soya bean adhesives was issued to researcher Otis Johnson in 1923, although in fact it was the American industrialist Irving F. Laucks who pioneered the development of soya bean-based glues in the early years of the 20th century.[3] Laucks began selling his soya bean glue in 1923 as an improvement over the often-used casein glue systems. Although not

In Brief

- **In 2008, the world produced an estimated 221m t of soya beans, largely for their oil and protein-rich meal**
- **The first US patent for soya bean adhesives, made by denaturing soya flour, was issued in 1923**
- **Interest in soya adhesives is being revived owing to new legislation curbing emissions of formaldehydes**
- **New technologies to improve soya adhesive properties involve combining them with other ingredients**



Ready to roll: a commercial roller coater prepares to apply renewable *Soya d* adhesive

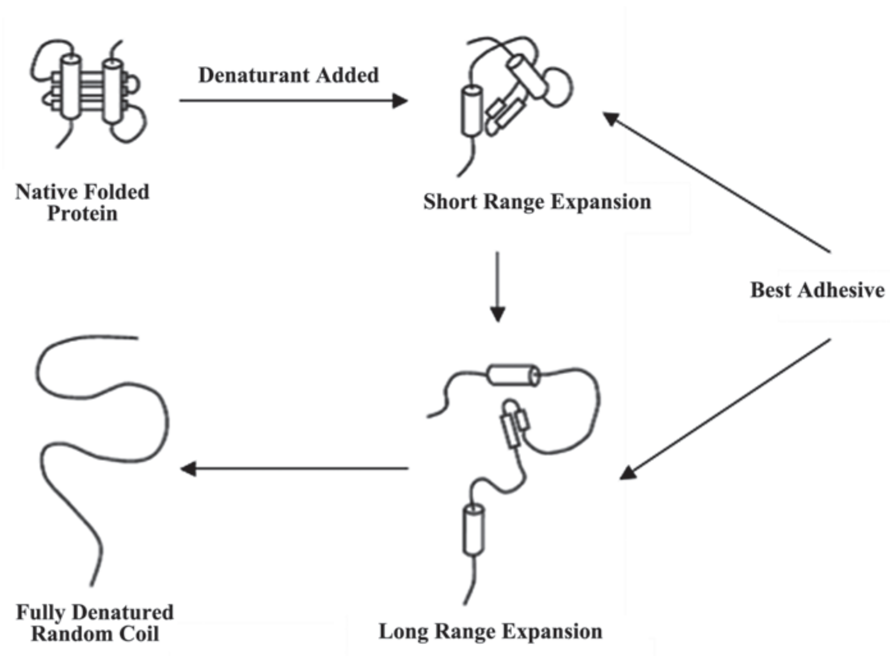


Figure 1: unfolding soya protein with alkali is critical to achieve good adhesive performance

durable outdoors, soya bean glues were considered to be acceptable for most interior applications. By 1927, most of the plywood industry was using Laucks' soya adhesive formulation, but the industry was still plagued by durability issues and the inability to perform under exterior conditions. This severely limited the growth opportunities for the plywood industry.

The majority of these early formulated soya flour adhesives were based on alkali denaturation. In this process, soya flour is dispersed in water followed by an alkali base addition.[4] Typically, sodium hydroxide was employed, but often calcium hydroxide was used in combination to improve the water resistance of the glue. It is generally accepted that exposure of soya protein to an alkali base causes the protein to undergo an 'unfolding' process, altering its structure to expose more hydrophobic groups buried inside the collapsed structure.

This unfolding or denaturing of the protein (Figure 1) is critical to achieve good performance from the adhesive. Because soya flour also contains large amounts of both soluble and insoluble carbohydrates, it is also expected that the carbohydrates will undergo some changes, contributing to the increased tack of the alkali-modified, denatured formulation. One of the shortcomings of this approach, however, is the limited pot life of the adhesive. After only a few hours, both the viscosity and performance of the soya adhesive begin to reduce. This is likely to be a result of excessive denaturation coupled with some protein hydrolysis, although at room temperature the latter should not be too significant.

Water-durable glue

Adhesive developers and formulators began modifying their adhesives with various additives as a result of a new commercial standard adopted in 1938. The partial replacement of sodium with calcium, along with the addition of sodium silicate, was the most common approach. Soon afterwards, the addition of blood protein to the soya adhesive formulation became important.[5] This improved the water resistance of plywood panels and, most importantly, improved the performance of the glue-line such that it was capable of passing the new standard. Although the odour of blood made this an unpopular choice, the inclusion of blood into soya formulations was well accepted and proved to be a very successful solution for 25 years.

Wood flooring: made with soya adhesive

However, the plywood industry was still in dire need of a truly water-resistant glue-line. The researcher James Nevin at Harbor Plywood filled that void with the introduction of phenol-formaldehyde (PF) adhesives[3] in 1934 – a development that transformed the exterior plywood industry. Even today, the majority of exterior grade plywood is still produced from PF resins.

Urea-formaldehyde (UF) adhesives were first introduced in 1937, but soya and soya–blood still enjoyed the dominant position for interior panels for the next 20 years. It was not until the late 1950s that UF glues began to supplant soya adhesives on a routine basis. These fossil fuel-based adhesives – urea from natural gas and formaldehyde from methanol – simply became much easier to use; they enjoyed longer pot lives, less colour, higher solids, and lower viscosity, along with a lower price. By then, UF adhesives were the clear choice for interior panel producers and soon led to the nearly complete demise of soya bean use in wood adhesives.

Particleboard (PB) was developed during World War II using phenolic glues, but interior PB was also an attractive market for UF adhesives. Medium density fibreboard (MDF), introduced in 1965, also used UF adhesives. Durability issues aside, neither PB nor MDF could be feasibly produced with soya bean technology at that time because they require a high-solids, low-viscosity adhesive.

Soya bean re-birth

Through the early years of UF chemistry, it became well accepted that the more formaldehyde in the formulation, the better and faster the UF adhesive would perform. Unfortunately, this discovery also led to higher emissions of formaldehyde from the final product. The use of UF glues in interior applications led to health concerns over formaldehyde emissions from these products. Thus, beginning in the 1970s and continuing through today, the acceptable level of formaldehyde emissions from composite panels has been decreasing. This culminated in the 2007 California Air Resource Board's (CARB) acceptance of vastly reduced emissions levels for any panel sold in the state of California.[6]

In July 2010, the US Congress passed a law that essentially makes the CARB levels a national standard by the year 2013. These formaldehyde emission concerns, coupled with higher fossil fuel prices, have led to a renewed interest in the development of better performing and lower cost soya-based adhesives.

In 1998, Roland Kreibich at Kreibich Associates discovered that highly denatured and partly hydrolysed soya flour-based adhesive, termed soya hydrolysate, was a highly effective ingredient in a two-part system for wood finger joint bonding. This process, commonly referred to as the 'honeymoon' system, applied a phenol resorcinol formaldehyde (PRF) on one side and the soya hydrolysate on the other, then joined the pieces together at room temperature to form a very strong and durable bond, even with undried wood.[7]

With the price of phenol skyrocketing in the early 2000s, this was an opportunity for a partial replacement of phenol formaldehyde (PF) with a low

Table 1: A typical soya bean comprises high concentrations of lipids oils and protein

Part	Protein	Lipid (oil)	Carbohydrate	Ash
Typical	40	20	35	5.0
Range	39.5-50.2	16.3-21.5		
Protein+Oil Range	59.7-67.5			

Source: Reference 1.

Table 2: Soya meal and estimated adhesive volumes for interior composite wood products

Region	Soya meal (m t)	Interior glue (m t)	% of soya
US	42.5	1.5	3.5
Global	117.5	7	6.0

Source: Reference 2.

cost soya-based extender. Several groups showed the potential for this technology. However, soon afterwards, the price of phenol dropped precipitously. It is expected that when the global economy recovers and the price for the petroleum-based phenol increases, some of these soya bean adhesive extender technologies will become commercially successful.

In 2002, Kaichang Li from Oregon State University, US, discovered that when soya flour was combined with a well known paper wet strength additive, polyamidoamine epichlorohydrin (PAE), the 'wet strength' of the adhesive – a measure of how well the bond performs when wet – was substantially improved.

Most importantly, the bond durability using this technology was suitable for commercial production of interior plywood while meeting all of the current performance standards. These glue-line durability requirements are very similar to those first introduced in 1938, but the reintroduction of the early solution of blood inclusion is very unlikely today!

The PAE-soya discovery was considered to be a huge step forward in adhesive technology offerings, not only in the development of a primarily bio-based adhesive, but also of a new formaldehyde-free adhesive. A patent was issued on this application in 2007. The use of formaldehyde-free adhesives is essential to the production of 'no added formaldehyde' (NAF) panels, a new classification of low-emitting composite panels.

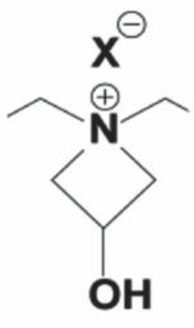


Figure 2: azetidinium functional group

The soya-PAE chemistry is based on the reactive functional azetidinium of the PAE polymer. The azetidinium ion (Figure 2) is capable of reacting with several side groups of the protein amino acids, which make up the protein. One proposed bonding mechanism involves the reaction of PAE with the amine end group of the amino acid lysine in soya flour. The amount of PAE in the formulation is dependent on both the desired degree of water resistance needed and also on the product composition. Typically the PAE is added at levels from 10 to 30% of the total solids of the formulation.

US chemical company Hercules was the producer of PAE and obtained the exclusive rights to the resulting so-called Li technology. In 2005, the largest hardwood plywood producer in North America, Columbia Forest Products (CFP), began converting all of its commercial operations over to this new soya-PAE system. Today, CFP has completed the conversion of all of its facilities and sells the panels under the *Purebond* trademark.

In 2006, Hercules partnered with the soya adhesive specialist, Heartland Resource Technology, to advance this technology and to develop a line suitable for applications in the particleboard and medium density fiberboard markets. Ashland acquired Hercules in 2008 and today sells a soya adhesive product line under the trade name of *Soya d*. The *Soya d* technology now includes both PAE and non PAE-based technology and has experienced significant growth and technical advancement.

The soya–PAE adhesive is very homogeneous, lightly coloured and opaque. One of the challenges of working with soya flour in any soya formulation is the shear-thinning nature of the adhesive; that is, the adhesive's viscosity decreases as the shear rate increases. Many of the systems are also thixotropic – they thicken when not agitated – which can lead to pumping or transfer issues if process controls are not rigorously followed. The picture on page 22 demonstrates the excellent bond quality of a variety of different engineered wood flooring compositions; shown after being subjected to the three-cycle soak and dry test.

The *Soya d* progression in particleboard and MDF has been slower than for plywood because of the more restrictive processing requirements of low viscosity, so it can be spray applied, and high solids content. The latter is a result of a need to minimise total mat moisture going into the press to avoid excessive gas pressure build-up and panel delamination when the press opens.

Typically, in addition to the modified soya flour and PAE, *Soya d* for PB and MDF also contains a dispersion diluent to aid in the solvation, distribution, and total solids of the final formulation. Soya has also been shown to function as an effective extender/co-adhesive with poly(vinyl acetate) (PVAc) adhesives. Franklin recently introduced[8] *Multibond MX-100* and Hexion has successfully commercialised its *Ecobind* adhesives, which combine soya with PVAc and PF.

Other work in this space includes novel soya bean-modified adhesives or a co-adhesive system.[9,10] Although these approaches have not yet enjoyed the commercial success of the Li invention, they do exemplify the large activity and options that exist today in the exciting area of soya bean-based glues.

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