

Adhesives and plastics based on soy protein products

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Abstract

Significance of eco-friendly materials based on easily renewable natural resources, and the finite nature of petrochemical resources, has necessitated the development of polymers from agricultural processing by products such as soy proteins from oil processing. Although, considerable work was done in the early part of last century on polymers based on soy protein, there was almost no activity in this field for the last fifty years. There is a need to critically analyse the available literature on soy protein based polymeric materials. Therefore, an attempt is made to review the state-of-the-art of the polymeric materials with emphasis on adhesives and plastics derived from soy protein, a renewable resource abundantly available in nature.

Keywords: Soy proteins; Adhesives; Modification; Soy plastics

Abbreviations: NDI, nitrogen dispersity index; NSI, nitrogen solubility index; cP, centipoise; GH, guanidine hydrochloride; SDS, sodium dodecyl sulphate; SDBS, sodium dodecyl benzene sulphonate; Tg, glass transition temperature; DMS, dynamic mechanical spectroscopy; DSC, differential scanning calorimetry; RG, rich globulin; UF, urea-formaldehyde; PGA, propylene glycol alginate; MPa, mega pascal; GPa, giga pascal; S, Svedberg ($1\text{S} = 10^{-13}\text{s}$); kDa, kilo dalton; MDI, methylene diphenyl diisocyanate; TMSP, trypsin modified soy protein; SPC, soy protein concentrate; SPI, soy protein isolate; N, Newton; Psi, pounds per square inch.

1. Introduction

Soybean is primarily an industrial crop cultivated for oil and protein. Despite the low oil content of the seed ($\sim 20\%$ on moisture free basis) soybeans are the largest single source of edible oil and account for $\sim 52\%$ of the total oil seed production of the world. With each ton of crude soybean oil, approximately 4.5 tons of soybean meal (protein content $\sim 44\%$) is produced. For each ton of soybean processed, the commercial value of the meal obtained usually exceeds that of the extracted oil. Despite considerable public and commercial interest in soybean prod-

ucts as food, the proportion of soy protein consumed directly in human nutrition and other industrial uses is really small and there is a need to look for the new industrial uses of soy protein. Bulk of soybean meal is used in animal feeds for the production of meat and eggs (Berk, 1992).

U.S. and Brazil account for most of the soybean production. According to FAO estimates over 160 million tonnes of soybean was produced worldwide in the year 2000. The leading producer was the USA, which accounted for 49%; Latin America and the Caribbean produced 34%, Asia 14% and Africa less than 1% (Ph (Post harvest) Action News, 2001, FAO). An important development was the considerable improvement in the yields through plant breeding and advanced agro-technical practice.

Soy-based plastics (Paetau et al., 1994a,b; Wang et al., 1996; Jane and Wang, 1996), adhesives (Kalapathy et al., 1995), films (Shih, 1994; Stuchell and Krochta, 1994) and coatings are being considered for applications such as agricultural equipment, automobiles, marine infrastructure and civil engineering (Wool, 1999; Wool et al., 2000a; Coggeshall, 1999; Paul and Krinski, 1983). To overcome the shortage of wood, the construction industry is interested in the production of panel products using renewable agricultural resources such as wheat or soybean straw etc (Wildes, 2001). They are considered to be excellent fibres for panel products. There is also a need to develop eco-friendly polymeric materials using renewable resources. Plywood industry needs environment-friendly adhesives from renewable resources because petroleum resources are finite and are becoming limited, whereas the demand for adhesives is increasing (Kalapathy et al., 1995). On the other hand, abundant proteins are available from renewable resources and agricultural processing by-products such as soybean proteins from oil processing. Utilisation of these protein by-products as biodegradable adhesives and resins will help to overcome environmental problems and add value to agricultural by-products.

Soy protein based adhesives were first developed in 1923 when a patent was granted for soybean meal-based glue (Johnson, 1923). By the late 1920s, soy proteins were used in many indus-

trial products, such as adhesives for wood and paper, binders in coatings and paints and as emulsifiers in colloidal rubber products (Lambuth, 1994; Wood Handbook, 1987; Burnett, 1951; Schwalbe, 1961; Bain et al., 1961; Myers 1993). Other industrial soy-based products that came in the 1930s and 40s included textile fibres, foams for fire extinguishers, plastics and lubricants.

However, the availability of petroleum at a lower cost and biochemical inertness of petroleum-based products proved disastrous for the industrial use of soy. It is only after the lapse of almost 50 years that the significance of eco-friendly material has been realised and once again, the polymer scientists are looking at nature for developing adhesives, plastics, composites, elastomers from soybean. In this paper, an attempt is made to review the state-of-the-art of polymeric materials based on soybean protein with emphasis on adhesives and plastics derived from renewable resources available abundantly in nature.

2. Properties of soybean protein

The bulk of soy proteins are globulins, characterised by their solubility in salt solutions. The solubility of soy proteins in water is strongly affected by the pH. About 80% of the protein in raw seeds or unheated meal can be extracted at neutral or alkaline conditions. The pH dependence of solubility is used in the manufacture of isolated soybean protein. As the acidity is increased, solubility drops rapidly and a minimum is observed at pH 4.2–4.6. This is the isoelectric region of soybean proteins taken as a whole. Ultracentrifugation, gel filtration and electrophoresis can also be used for more precise fractionation (Kinsella, 1979).

The soy protein fractions have also been characterised by their sedimentation constants. Two major fractions, known as 7S and 11S have been studied extensively (S stands for Svedberg units). The numerical coefficient is the characteristic sedimentation constant in water at 20 °C. The content of 11S is around 52% and of 7S is 35%

(Kinsella, 1979). The other minor fractions have been designated as 2S (8%) and 15S (5%). The DSC scans of 7S and 11S fractions with 10% water content showed an endothermic transition at 120–150 °C, respectively (Wang et al., 1996).

The 2S fraction consists of low molecular mass polypeptides (in the range of 8000–20,000 Da) and comprises mainly the soybean trypsin inhibitors. The 7S fraction is highly heterogeneous. Its principal component is beta-conglycinin, a sugar containing globulin with a molecular mass in the order of 150–190 kDa. The fraction also comprises enzymes (beta-amylase and lipoxygenase) and hemagglutinins. The 11S fraction consists of glycinin, the principal protein of soybeans. Glycinin has a molecular mass of 320–360 kDa. 11S is a quaternary structure composed of three acidic and three basic subunits of ~35,000 and 20,000 Da with isoelectric points between pH 4.7–5.4 and 8.0–8.5, respectively. The polypeptides in native glycinin are tightly folded and stabilised via intermolecular disulphide bonds. The ability of soy proteins to undergo association–dissociation reactions under known conditions, is related to their functional properties and particularly to their texturisation. The 15S protein is probably a dimer of glycinin.

Conglycinin and glycinin are storage proteins and they are found in the protein bodies within the cells of the cotyledons (Kinsella, 1979).

Soy protein consists mainly of the acidic amino acids (aspartic and glutamic acids) and their corresponding amides (asparagine and glutamine), non-polar amino acids (alanine, valine and leucine), basic amino acids (lysine and arginine), uncharged polar amino acid (glycine) and approximately 1% of cystine (Table 1).

3. Soybean protein products

Soybean protein materials, which are useful for forming protein adhesives, are soy flour, protein concentrate, and, most preferably soy protein isolate. The soybean starting material is

Table 1
Amino acid composition of soybeans (Berk, 1992)

Amino acid	Composition g/16 g nitrogen
Isoleucine	4.54
Leucine	7.78
Lysine	6.38
Methionine	1.26
Cystine	1.33
Phenylalanine	4.94
Tyrosine	3.14
Threonine	3.86
Tryptophan	1.28
Valine	4.80
Arginine	7.23
Histidine	2.53
Alanine	4.26
Aspartic acid	11.70
Glutamic acid	18.70
Glycine	4.18
Proline	5.49
Serine	5.12

either soybean meal, flakes, cake or chips. The processing of Soybean seeds includes cleaning, drying, cracking, dehulling, flaking and extraction of oil by using hexane (Fig. 1) (Seal, 1980). The residual soybean meal, which contains some hexane, is then used for the production of defatted soybean meal, soy protein concentrates and soy protein isolates (Krinski and Scacciaferro, 1998). The composition of all the three soybean products is given in Table 2.

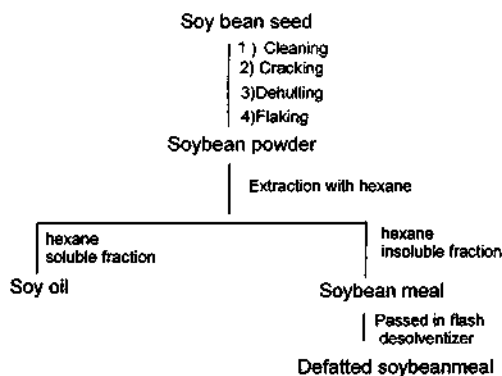


Fig. 1. Flow diagram for the production of defatted soybean meal.

Table 2
Composition of different soy protein products (Kinsella, 1979)

g/100 g product	Soy flour	Soy protein concentrate (SPC)	Soy protein isolate (SPI)
Protein (as is)	48	64	92
Fat (min)	0.3	0.3	0.5
Moisture (max)	10	10	<5
Fibre (crude)	3.0	4.5	<1
Ash	7	7	4
Carbohydrate	31–32	14–15	–

3.1. Soy flour

Soy flour is finely ground, defatted meal made from soybean containing less than 1% oil and a protein content ranging from 40–60% with a particle size less than 100 mesh (Krinski and Scacciaferro, 1998).

3.2. Defatted soybean meal

Defatted soybean meal is obtained by removing fatty acid or oil from soybean meal by using hexane as solvent (Fig. 1). After extraction solvent is removed (Seal, 1980).

The soluble protein contents are expressed in terms of their Nitrogen Solubility Index (NSI) or Protein Dispersibility Index (PDI). These indices express the percentage of the total content of nitrogen and protein, respectively. They also indicate the extent of protein denaturation and hence, the intensity of heat treatment which has been applied to the starting material. The particle sizes range from grits (or flakes) of varying sieve specification to fine powders and the PDI range from 10–90.

3.3. Soy protein concentrates

The flow diagram for the production of soy protein concentrate is given in Fig. 2. Three methods are commonly used to make soy protein concentrates (i) moist heat/water leach (Seal, 1980); (ii) aqueous alcohol (20–80% concentration) leach (Seal, 1980); and (iii) dilute mineral acid (usually hydrochloric acid) (Sair, 1959).

The first two methods denature the protein, which renders it insoluble. Both moist heat/water

leach and the aqueous alcohol leach processes employ a step in which there are no acidifying and neutralising steps. The concentrates produced by the above two methods have a low PDI in the range of 10–15%.

The third method, devised by Sair (1959), hinges on isoelectric point of the major globular soy proteins, which lies between pH 4.2–4.5. At this pH, 90% of the proteins are insoluble. This process does not denature the proteins and a high PDI (60–70%) in the finished product is ensured. The water-soluble fraction is discarded.

3.4. Soy protein isolates

The most commonly produced isolates have high soluble protein contents, PDI of 80–90%, and as a consequence, are highly-valued functional additive.

The general method of production adopted by commercial manufacturer utilises the isoelectric point of the soy proteins (Fig. 3). Defatted soy flake is stirred into warm water and pH is raised to between 7 and 8.5 by the addition of alkali such as sodium hydroxide. The solution, which contains the protein and soluble carbohydrate fractions, is separated from the insoluble fraction by centrifugation. The pH of the solution is lowered to 4.2–4.5 by the addition of hydrochloric acid, the soluble sugars are washed away and the precipitated protein rich residue is obtained, which is neutralised and freeze dried. Soy protein isolate obtained is a creamy-coloured powder and on analysis yields a protein content of 90–95% (on a dry weight basis) and a PDI in the range of 80–90% (Seal, 1980).

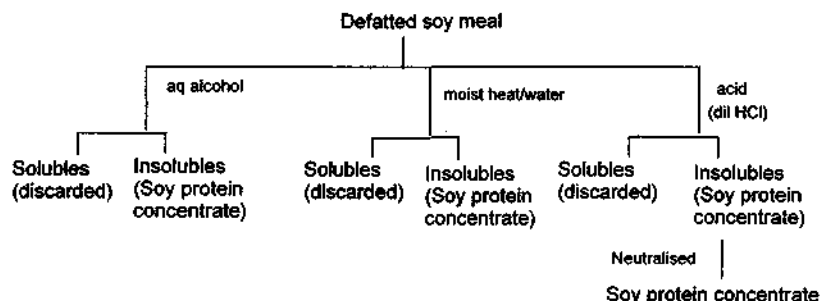


Fig. 2. Flow diagram for the production of soy protein concentrate.

4. Performance of soy protein adhesives

The adhesive performance of soybean proteins is dependent upon the particle size, nature of surface, structure of protein, its viscosity and pH (Lambuth, 1977). Other factors, which can affect their performance, are the processing parameters such as press temperature, pressure and time (Lambuth, 1977).

4.1. Particle size

The particle size of the soybean meal used for adhesive has a significant effect on its suitability and performance. Fineness of the grind is often expressed in terms of specific surface area (cm^2/g according to standard test) than mesh size. A specific surface area of 3000–6000 cm^2/g is considered to be satisfactory for adhesive grade or in other words, at least 97% should pass through a 325-mesh screen (Lambuth, 2001).

4.2. Nature of surface and substrate

Adhesive properties are also dependent upon the nature of surface to be bonded. If the surface is too rough, it will cause a cohesive failure and if the surface structure is too smooth, it will cause an adhesive failure (Mackay, 1998). The bonding between adhesive polymers and wood polymers is mostly caused by a combination of mechanical adhesion (interlocking by adhesive penetration through porous wood surfaces) and molecular attractive forces (van der Waals forces, hydrogen bonds). Rough surface structure produces a ran-

dom micro 'finger joint' structure under pressure whereas, too smooth a surface might have less micro random 'finger joint' effects, which may be responsible for the low gluing strength. Kalapathy et al. (1995) observed highest strength with soft maple wood (280 N) whereas, it was lower with hard wood such as walnut (135 N) and zero or very low strengths with yellow pine (0 N) and poplar (71 N) soft woods. Since the composition of major components of woods vary little from wood to wood this variation in adhesive strength with the type of wood may be due to the variation in physical properties of woods, such as porosity and degree of surface roughness (Tarkow, 1979). Moisture content of the substrate can also affect the adhesive strength.

Adhesive strength is also dependent upon the type of substrate wood, paper, metal etc.

4.3. Viscosity

Viscosity is an important property, which largely governs the adhesive behaviour (Lambuth, 1997). The operating viscosity limits of soybean

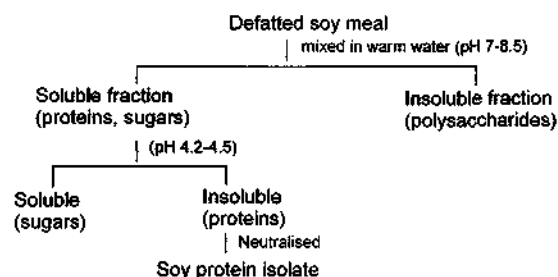


Fig. 3. Flow diagram for the production of soy protein isolate.

glues are very large ranging from 500 to 75,000 cP depending upon the application and the nature of the materials to be glued. A viscosity of 500–5000 cP is needed for gluing materials which are highly absorbing such as paper, soft board and dried wood aggregates, 5000–25,000 cP for most wood laminating purposes (both cold or hot press) and over 50,000 cP for mastic consistency wood laminating operations. A viscosity range of about 8000–20,000 cP has been specified for no clamp cold press technique.

The high viscosity soybean proteins result from increased intermolecular interactions due to unfolded protein molecules. The major forces that facilitate such interactions are electrostatic and covalent disulphide bonding. Ionic environments have been known to weaken the electrostatic interactions between protein molecules. Thus the viscosity of protein can be varied by treating with salts or by using reducing agents without affecting the adhesive strength or water resistance. Enzymatic or alkaline hydrolysis also reduces the viscosity. Higher the pH, higher will be the rate of hydrolysis, better adhesive strength and water resistance but short storage life. At higher pH, viscosity decreased with storage time and adversely affect the adhesive properties. A moderate pH/temperature combination of 10.0/50 °C has been recommended for better performance (Kalapathy et al., 1996; Hinterwaldner, 1997).

4.4. Structure of protein

The adhesive strength of protein glue depends on its ability to disperse in water and on the interaction of apolar and polar groups of the protein with wood material. In a native protein, the majority of polar and apolar groups are unavailable due to the internal bonds resulting from van der Waals forces, hydrogen bonds and hydrophobic interactions. For this reason a simple paste of soy flour is a poor adhesive and a chemical change is required to break the internal bonds and uncoil or disperse the polar protein molecules.

Dispersion and unfolding of protein are enhanced by hydrolysis or by increasing the pH to about 11 or higher (Lambuth, 1977). Treatment with sodium hydroxide unfolds the protein

molecules exposing the polar and apolar groups which in turn can interact with wood thereby leading to an improvement in the adhesive strength and improved water resistance (Lambuth, 1977) but at the same time shortens the useful life.

4.5. Processing parameters

The effect of press conditions such as pre-pressing drying time, protein concentration on gluing strength and water resistance of soybean protein adhesives in fibre cardboard applications has been reported recently (Zhong et al., 2001). An increase in shear strength was obtained with an increase in press time (1–10 min) and pressure (0.4–4 MPa) at 25 °C. The shear strength also increased with increase in temperature from 25 to 100 °C. Adhesive strength increased with increasing concentration up to an optimum limit. Too high concentration of glue gives high viscosity, which has poor flow and was not easy to spread whereas, too low concentration can easily penetrate the porous structure and is not available on the surface for gluing. The shear strength of SPI adhesives on fibre cardboard was affected significantly by the ratio of SPI/water and reached a maximum value at 12:100 (w/w).

For making an adhesive for wood or paper, soy flour is first wetted with water. It is then solubilised or dispersed by reacting with strong alkali such as sodium hydroxide or trisodium phosphate. During initial wetting, alkali is avoided otherwise it leads to the formation of permanent lumps. Treatment with alkali also helps to: (a) unfold the protein structure thus exposing all functional sites for interaction with wood; and (b) enhances the hydrolysis reaction which in turn affects the viscosity as well as the adhesive efficiency. The working life is only 6–8 h dependent upon the pH and the concentration of alkali.

The effect of temperature, time and pH of the medium on the adhesive properties has been investigated by Hettiarachchy et al. (1995). The optimum treatment conditions (pH/temperature) for producing alkali modified soy protein (AMSP) with the highest adhesive strengths were 9.0/70, 10.0/50, 11.0/50 and 12.0/40 °C. At higher pH i.e.

Table 3
High and low-alkali formulation process for soy glues (Lambuth, 2001)

Component	High alkali (pbw)	Low alkali (pbw)	Extracted soy protein based (pbw)
Water at 60–70 °F	175	225	385
Adhesive grade soybean flour	97	97	100 ^a
Pine oil or diesel oil defoamer (mix until smooth)	3 ^b	3 ^b	1 ^b
Water at 60–70 °F (mix until smooth)	145	150	–
Fresh hydrated lime as a slurry	12	30	–
50% NaOH	14 (mix for 1 min)	–	6 (mix for 15 min)
China clay	–	–	100
Powdered sodium sulphite	–	–	1
Sodium silicate solution (mix 1 min) ^c	25	–	–
<i>o</i> -Phenyl phenol (mix 10 min)	5	–	–
Hexamethylene tetramine	–	–	3
Water at 60–70 °F (mix 5 min)	–	50	6

pbw stands for parts by weight.

^a Extracted soybean protein or blend.

^b Normally blended with soy flour/or extracted soy protein for dust control.

^c 8.90% Na₂O, 28.7% SiO₂; it increases the water holding capacity levels the viscosity and prolongs the useful life of glues.

between 11.0 and 12.0 alkali present in the glue reacts with wood and causes discoloration (brown). It is also called alkali stain. Such a glue line discoloration has limited the use of soy glues in fine furniture and paper products. Hence, a moderate pH/temperature combination of 10.0/50 °C is preferred. Mild alkaline agents, such as calcium hydroxide, borax, disodium phosphate, ammonium hydroxide, etc., can give stainless glues but have poor adhesive strengths (Lambuth, 1977). They can be used for less demanding applications such as paper coating or soft board etc. Mixed alkalis (e.g. mixture of NaOH and Ca(OH)₂ or magnesium salt) have been used to improve water resistance and the assembly time tolerance of soybean adhesives by reacting with protein constituents to yield insoluble proteinates and altered glue consistency (Lambuth, 1977).

Such adhesives need preservatives to provide mold resistance at high humidities. Without this, even heat-cured soybean adhesives will show a mold growth when the moisture content of bonded wood is ~ 20%. Copper naphthenate, *ortho* phenyl phenol, copper-8-quinolinolate are the preservatives used. Some chlorinated phenols can also be used. The optimum concentration lies in the range of 1–2.5%.

The major advantage of soy glues is that they can be cured either hot or cold (Lambuth, 1994). Hot-curing can be done at temperatures between 230 and 270 °C, pressure of 1.21 MPa and curing time of 1.5 min to prepare plywood panel of one-quarter inch thickness. Curing conditions can be varied depending upon the thickness of plywood panel. Another advantage of soy glues is that they can be used to bond green lumber without kiln drying. On dry wood, cold-curing of soybean glues is recommended at a pressure of 1.03–1.21 MPa for 15 min. During the initial clamping, soybean glues form a film having sufficient gel strength by dehydration into dry wood to hold the plies tightly even after removal of pressure. Complete adhesive cure is obtained at room temperature over several days but machining can be done after 6 h. This process is called as no-clamp process. High- and low-alkali formulations are given in Table 3. Sodium silicate and hydrated lime are added in the high-alkali mix to maintain viscosity of glue for longer duration and improve water resistance by forming some insoluble proteinates. The major disadvantages of soybean protein based adhesives are low gluing strength and poor water resistance (Lambuth, 1994). It is therefore, necessary to modify soybean proteins to improve their performance.

5. Modification of soy proteins

Improvement of functional properties of protein by altering their molecular structure or conformation through physical, chemical or enzymatic agents at the secondary, tertiary and quaternary levels has been well documented in the literature (Feeney and Whitaker, 1977, 1985).

The modification of soy proteins has been carried out to develop adhesives (Market opportunity summary, 2000) for the larger wood-composite market or for agro-composites based on renewable resources having:

1. An improved water-resistance to replace the urea-formaldehyde and phenol-formaldehyde resins.
2. Soy flour/methylene diphenyl diisocyanate mixture for improved economics and worker safety.
3. Soy/phenol-resorcinol-formaldehyde adhesive system especially for finger-jointing the green lumber.

Denaturing and disulphide bond cleavage of proteins are expected to enhance the adhesive performance and water resistance by unfolding the protein molecules and increasing the interaction with wood substrate (Kinsella, 1979; Kalapathy et al., 1997). The decrease in viscosity enhances the flow of glues and its penetration as well as spreading and foaming necessary for wood adhesives.

Crosslinking, acylation, oxidation, reaction with alkoxy silane and copolymerisation are other methods used for modification of soy protein (Lambuth, 1977; Franzen and Kinsella, 1976; Krinski and Steinmetz, 1987a,b).

5.1. Denaturation and cleavage of proteins

Methods normally used to denature proteins include: exposure to heat, acid/alkali, organic solvents, detergents and urea (Wu and Inglet, 1974). Soy proteins have been modified using alkali (NaOH) (Mackay, 1998; Hettiarachchy et al., 1995) and proteases such as trypsin, pepsin, papain, alcalase (Chae et al., 1997; Hamada and Marshall, 1989; Sun and Bian, 1999a). Certain

reagents such as urea, guanidine hydrochloride (GH), sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulphonate (SDBS) denature protein as well as improve the gluing strength and their water resistance (Huang and Sun, 2000a,b; Bian and Sun, 1998; Burnett and Eichenberger, 1948).

Alkali-modified soy protein adhesive was reported to be stronger and more water resistant compared with adhesive containing unmodified soy protein (Hettiarachchy et al., 1995). Racemisation of L-amino acid to D-isomers has been reported to occur on exposing soy proteins to strongly alkaline conditions (pH up to 14) (Friedman and Liardon, 1985). Alkaline treatment also helps in unfolding the protein molecules and exposing the polar groups for interaction. Treatment with alkali improved the film appearance without affecting properties such as water vapour permeability, oxygen permeability and tensile strength (Brandenburg et al., 1993), thereby enhancing its use as edible packaging material. Divalent cations have been used to modify the gelling characteristics of soy protein dispersed using mild alkali (Tanford, 1968).

The effect of varying concentrations of urea and guanidine hydrochloride on adhesion property of modified-SPI adhesives was investigated by Huang and Sun (2000a). Soy protein modified by treatment with 1 and 3 M urea showed greater shear strengths in comparison to unmodified SPI. In the case of guanidine hydrochloride-treated SPI (GH-SPI), the isolate treated with 0.5 and 1 M guanidine hydrochloride (GH) gave greater shear strength than unmodified SPI.

Huang and Sun (2000b) evaluated the adhesive and water resistance properties of SPI modified by varying concentration of sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulphonate (SDBS). SPI modified by 0.5 and 1% SDS or SDBS showed greater shear strength than unmodified SPI. Urea-modified SPI adhesive was better in terms of shear strength and water resistance as compared with alkali-modified SPI (Sun and Bian, 1999a). The concentrations of urea or

GH had a significant effect on the extent of protein unfolding and, ultimately, on the adhesive properties. Compared with urea and GH, SDS- and SDBS-modified SPI have increased water resistance, as well as improved adhesive strength. All these treatments lead to the denaturation of proteins. However, SDS or SDBS denaturing agents impart some unique properties such as high shear strength, better water resistance and zero delamination (Huang and Sun, 2000b).

Wet and dry heat, grinding, freezing, pressure, irradiation and high frequency sound waves can also be used for denaturing proteins. However, the adhesive properties of soy are degraded when subjected to these conditions. Organic solvents can denature proteins but increase the cost of processing (Lambuth, 1977).

Soy proteins have also been modified by using salts (such as NaCl, Na₂SO₄) or reducing agents (such as Na₂SO₃). A decrease in soy protein viscosity was reported upon addition of ionic salts and disulphide reducing agents (Petruccelli and Anon, 1995; Circle et al., 1964). Shen (1976) reported that at high pH, apart from denaturation some other reactions also occur which enhances the solubility. Ionic environments weaken the electrostatic interaction between the protein molecules by electrostatic shielding. The effect of ionic strength on the functional properties of soy proteins, such as emulsification, foaming, water binding and gelation has been well reported by Kinsella and co-workers (Kinsella, 1979; German et al., 1985; Klemazewski and Kinsella, 1991; Kella et al., 1998). Viscosity and adhesive strengths decreased with increasing concentrations of salts. At concentrations of 0.1 M, NaCl/Na₂SO₄/Na₂SO₃ reduced the viscosity of soy proteins with no significant adverse effect on adhesive strength and water resistance (Kalapathy et al., 1996). Viscosity was reduced from > 30,000 to 6000/1050 cP in the presence of 0.1 M NaCl/Na₂SO₄. The Na₂SO₃ treatment (0.1 M) gave an isolate with the lowest viscosity 110 cP and 28% decrease in disulphide linkages. Further increase of salt concentrations resulted in a decrease in viscosity with a consequent decrease in adhesive properties. According to Petruccelli and Anon (1995) there was the disappearance of high molec-

ular weight aggregates on treatment with Na₂SO₃. Catalyst (Cu) and oxygen was added to study the sulphitolytic of soy protein isolate. It was observed that AB-11S subunit of glycinin were reduced when urea was used. Components, other than AB-11S subunit was reduced in presence of Cu and/or oxygen.

Reducing agents, such as sulphites, cleave the inter- and intra-disulphide bonds in protein molecules. The presence of disulphide bonds in native protein molecules affects their flexibility and unfolding properties. Cleavage of disulphide bonds by reducing agents leads to an increase in surface hydrophobicity, foaming capacity and foam stability (Kim and Kinsella, 1986; Kawamura et al., 1985; Kalapathy et al., 1997). Spray- or freeze-drying showed no significant effect on molecular properties and functionalities of disulphide bond-cleaved soy proteins. The recommended concentration of all these denaturants lies in the range of 0.1 to 1%, based on the weight of soy flour (Shen, 1976).

5.2. Crosslinking

Sulphur compounds, such as CS₂, ethylene di- or tri-thiocarbonate, thiourea and potassium xanthate, are strong crosslinkers of dispersed soy protein. They have been used to improve their water resistance, working life and consistency (Bjorksten, 1951). Other crosslinking agents that can be used for alkaline soy dispersions are soluble copper, chromium (Kowarsky, 1955), zinc salts or aliphatic epoxies. Epoxies are active hardening agents for alkaline soy glues and yield products with improved strength and durability but are expensive (Lambuth, 1965).

Addition of formaldehyde donors or adducts can crosslink or denature proteins and provide enhanced water resistance, longer useful glue life, granular consistency, improved assembly time tolerance and curing behaviour and increased water holding capacity (Lambuth, 1977). Examples of compounds of this group include: *tris*-hydroxymethyl nitromethane, dimethylol urea, sodium formaldehyde bisulphite, aldehydic starch, glyceraldehyde, hexamethylene tetramine, urea-formaldehyde, methylolated phenols etc. Formaldehyde

Table 4
Specificities of proteases (Simmonds and Orth, 1973)

Enzyme	pH optimum	Specificity
Pepsin	1.9	Fairly broad. Hydrolyses proteins and peptides, particularly those with bonds adjacent to aromatic or dicarboxylic L-amino acid residue
Trypsin	7-9	Hydrolyses peptides, amides, esters at bonds involving the carboxyl group of L-arginine or -lysine
Chymotrypsin	8-9	Hydrolyses peptides, amides, esters especially bond involving the carboxyl groups aromatic L-amino acids
Papain	5.5	Hydrolyses peptides, amides, and esters at bonds involving basic amino acids, leucine or glycine
Pronase	7-9	Wide

and paraformaldehyde are very active crosslinking agents and can cause pre-mature gelation. Therefore, very low concentration (i.e. in the range 0.1–1%) of aldehyde-active compounds is sufficient and is added during the final stage of the glue mix.

5.3. Enzyme modification

The advantages of enzyme modification include high reaction rates, mild conditions, and, most importantly, specificity. Proteases hydrolyse peptide bonds in proteins to modify their structure. The characteristics and specificity of some of the proteases available for industrial use are listed in Table 4.

Modification of soy protein isolate with papain was reported to affect hydrophobicity, solubility and emulsifying properties (Wu et al., 1998). Modified SPI had significantly higher solubility and emulsifying properties. Trypsin-modified SPI (TMSP) or soybean flour (Kalapathy et al., 1995; Ignjatovic et al., 1998) exhibited much higher adhesive strength on soft maple, compared with that of unmodified SPI (Table 5). Effect of the duration of heat treatment (at 120 °C) on the adhesive strength is given in Table 6. Initially the strength increased with increase in heating time (120 °C) up to 1 h followed by a decrease. Urea-formaldehyde could be partially substituted by trypsin-modified soybean adhesive. The highest value of shear strength was reached when 30% urea-formaldehyde (UF) adhesive was replaced by modified soy based adhesive.

5.4. Chemical reactions

The ease of protein acylation can be demonstrated by the treatment of soy protein with succinic anhydride or acetic anhydride (Franzen and Kinsella, 1976). During the reaction, pH is maintained between 7 and 8 with sodium hydroxide. Both succinylation and acetylation have been utilised to improve functional properties such as solubility, and surface hydrophobicity. The soy proteins are reduced with sulphur compounds such as ammonium thioglycolate followed by reaction with phthalic anhydride. Acyl-modified protein has been used as a binder for paper coating application (Coco et al., 1984) (Scheme 1).

Silanated SPI is produced by mixing alkaline soybean flake extract with alkoxy silanes such as γ -glycidyloxypropyl trimethoxysilane at 50 °C for

Table 5
Adhesive strength of trypsin modified soy protein (TMSP) with different types of wood after cold pressing (Kalapathy et al., 1995)

Sample	Adhesive strength (N)	
	Control	TMSP
Walnut	0	135
Cherry	0	195
Maple	50	284
Poplar	0	71
Yellow pine	0	0

Values are mean of three measurements, N (Newton). One mg/cm² protein concentration, cold pressed for 2 h and cured at ambient condition.

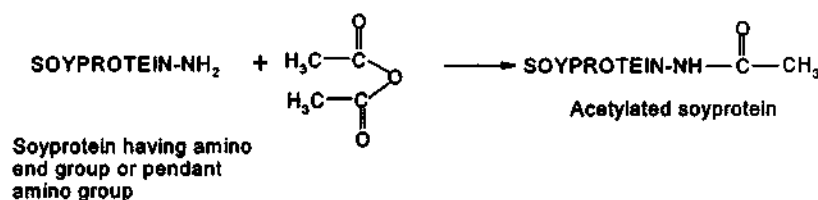
Table 6
Effect of duration of thermal treatment on adhesive strength (N) of TMSP on soft maple wood after hot pressing (Kalapathy et al., 1995)

Heating time (h) at 120 °C	Adhesive strength (N)	
	Modified protein	Control
0.25	476	263
0.5	482	344
0.75	493	388
1.0	617	614
1.5	578	656
2.0	475	697
2.5	495	736

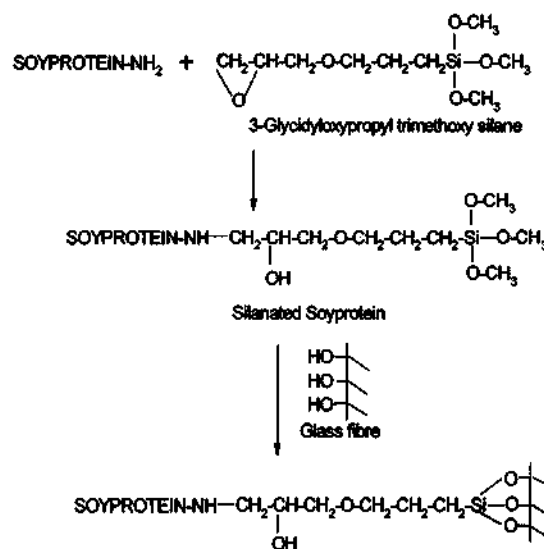
TMSP, trypsin modified soy protein.

1 h at pH 11. Modified protein was then separated by isoelectric precipitation using H_2SO_4 (Krinski and Steinmetz, 1987a). Silanated SPI was mixed with ammonium nitrate, clay and ammonium hydroxide and heated at 60 °C to give a binder, which is used as paper coating. Silanation using 3-(2-aminoethyl)-aminopropyltrimethoxy silane as a coupling agent enhances the interfacial adhesion between soy matrix and glass fibre in the production of fibre-reinforced composites (Liang and Wang, 1999) (Scheme 2).

Copolymers of SPI were prepared by heating an alkaline dispersion of SPI with cationic epoxide or acrylate monomer such as (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride/hydroxyalkyl acrylate/methacrylamidoglycolate methyl ether to give modified protein materials (Krinski and Steinmetz, 1987b). The pH was maintained at 10 at 10 °C during the reaction of SPI with hydroxy alkyl acrylate (Steinmetz and Krinski, 1987). Modification of SPI with alkyl acrylamido glycolate alkyl ether at 50 °C and pH 4.5



Scheme 1. Acylation of amino group of soy protein.

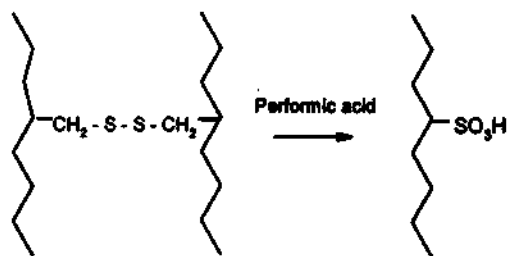


Scheme 2. Silanation of soy protein for improving interfacial adhesion in glass fibre reinforced composites.

was reported by Steinmetz and Krinski (1985). The modified protein could be used alone or in combination with styrene-butadiene rubber (SBR) latex for paper coating. It has a high affinity for pigments in paper coating compositions and gives paper having good ink receptivity and printability.

Vinyl monomers such as styrene or butyl acrylate on emulsion polymerisation using ammonium per sulphate as an initiator with SPI gave graft co-polymer, which is used in combination with other synthetic latex for coating applications (Dykstra and Hollingsworth, 1975).

Oxidised SPI with 50–70% of cystine residues can be modified by oxidation, which convert cystine to cysteic acid (Scheme 3). Such a protein can be used as a binder or adhesive in coatings for paper and paperboard, which comes in contact



Scheme 3. Oxidation of cystine.

with dry food, drugs and cosmetics (Rockville, 1982).

5.5. Interaction with polysaccharides

Formation of electrostatic/covalent complexes upon mixing SPI with sodium alginate/PGA (propylene glycol alginate) under alkaline conditions has been reported by Shih (1994). Films formed from covalent complexes had greater stability in water as compared to that obtained from protein–alginate complexes.

6. Blends of soy proteins

Adhesives with enhanced performance can be obtained by blending soy protein adhesives with other protein or synthetic adhesives. Blends of soy flour with blood, casein, phenol formaldehyde and phenol-resorcinol formaldehyde has been investigated with an aim to develop wood glues with unique combination of properties. The normal blending ratios were between about 20:80 and 80:20 soybean: blood or casein depending upon the properties required (Lambuth, 2001).

Table 7

Tensile strength and percent elongation for films prepared by the interaction of soy isolate with sodium alginate or propylene glycol alginate (PGA) (Shih, 1994)

Soy protein films	Thickness ($\times 10^{-2}$ cm)	Tensile strength (kPa)	Elongation (%)
With sodium alginate in absence of cyanoborohydride	1.55	821 \pm 90	15.5 \pm 0.9
With sodium alginate in presence of cyanoborohydride	1.78	1034 \pm 124	30.5 \pm 5.1
With PGA and pH 8	1.34	779 \pm 76	18.3 \pm 0.9
With PGA and KOH	1.47	848 \pm 69	22.8 \pm 1.5
With PGA, KOH and lauric acid	2.18	1158 \pm 138	20.5 \pm 6.0

Thickness was mean of five measurements. Tensile strength and elongation were the mean of three determinations.

Table 8

Typical formulation of a soy flour-blood 'blend glue' (Lambuth, 2001)

Component	Pbw
Water at 60–70 °F	180
Adhesive-grade soybean flour	62
93% soluble dried animal blood	25
200-mesh wood flour	10 ^a
Pine oil or diesel defoamer (mix 3 min)	3 ^a
Water at 60–70 °F (mix 2 min)	26
Fresh hydrated lime (as a slurry)	8
Water at 60–70 °F (mix 1 min)	16
Sodium silicate solution (mix 1 min) ^b	40
50% sodium hydroxide solution (mix 5 min)	10
<i>o</i> -Phenyl phenol (mix 1 min)	5

^a Normally blended with soybean flour and direct blood for dust control.

^b 8.90% Na₂O, 28.7% SiO₂.

6.1. Soybean-blood glues

Animal glues have proved useful as adhesives for wood. They have excessive water sensitivity. Blending with soybean resulted in completely hydrolysed glue. However, such glues soften on heating (Truax, 1929, Bulletin 1500). Blends of highly soluble spray-dried animal blood with adhesive grade soy flour (Tables 7 and 8) have been used extensively till 1960s. Such blended glues had improved adhesive properties and were ideal for wood product assembly. In such blends, blood provides water resistance and rapid hot cure, whereas soy flour provides the granular consistency required for machine application and assembly line tolerance (Lambuth, 2001). Blending also resulted in the cost reduction, as adhesives

based on blood were quite expensive. Soluble dried chicken blood blended with soy flour in the ratio of 1:1, crosslinked with dialdehyde starch have been used for manufacturing interior-type plywood (Weakley et al., 1972a). Soybean flour and soybean protein isolate blends showed pseudoplastic and thixotropic flow characteristics in the presence of dialdehyde starch. These blends when used for paper coating applications showed improved wax pick and wet-rub resistance (Weakley et al., 1972b).

6.2. Soybean-casein glues

Blends of adhesive grade soy flour with casein (ground or screened) have been prepared to obtain glues with composite performance for making panels and flush door assemblies (Hollow core flush doors, Report, 1983). Casein provides deep bond, tackiness and heat resistance whereas soy flour contributes granular consistency, which in turn helps in quick loss of water. Casein also provides a short clamping cycle cold cure. Such blended glues even maintain strong adhesion property in a fire until the glue lines are literally charred away. A single package adhesive formulation for use in Fire doors is given in Table 9.

6.3. Miscellaneous blends or composite adhesives

Composite adhesives for making plant fibre box for food have been obtained by blending soy protein isolate with varying amounts of poly (vi-

nyl alcohol) or poly (vinyl acetate) (Zhao et al., 2000; Brown, 1987). Blends of soy protein and phenolic resins are useful in finger-jointing of green lumber (Clay et al., 1999; Steele et al., 1998; Kriebich, 1995; Karcher, 1997). Such blends cure rapidly at room temperature, have excellent water resistance and reduced formaldehyde emission. Addition of soy protein, soy flour, soy hydrolysate and casein to OF resin resulted in a decrease in reactivity with increasing amount of protein without affecting the emission of formaldehyde (Lorenz et al., 1999; Ignjatovic et al., 1998). Vegetable protein-polyacrylate co-precipitate has been used as a binder/thickener for paper coating applications (Krinski and Hou, 2000).

7. Soybean based plastics

A study on soy protein plastics and soy meal blends with phenol formaldehyde (PF) resins for automotive applications was reported almost 60–70 years ago (Sue et al., 1997). At that time petroleum was expensive and soybeans were abundant. Soy products were introduced in phenolics primarily for cost dilution. The research efforts for the development of soy plastics have intensified in the last 15 years because of the increasing awareness about environment-friendly materials that are produced from annually renewable biodegradable resources. The potential uses of soy plastics as commodity products (spoon, bag, toys) have been successfully demonstrated (Paetau et al., 1994a,b; Wang et al., 1996, 1995). However, the main problems for commercialisation of these plastics are the price of the products and short-term as well as long-term performance of the material. Recent research efforts are directed towards solving these problems.

Paetau et al. (1994a), studied the effect of preparation and processing on mechanical properties and water absorption of biodegradable plastics prepared from soy isolate and concentrate. Water acts as a plasticiser and helps in the processing of soy proteins. Compression-molded specimens of soy isolate, protein concentrate, acid-treated soy isolate and acid-treated soy protein concentrate (moisture contents of 716.9%)

Table 9
Casein modified soy flour adhesives (Lambuth, 2001)

Dry glue composition	Pbw
'Adhesive grade' soy flour	58
60-mesh casein (precipitated using lactic acid)	19
Fresh hydrated lime	7
200-mesh wood flour	5
Granular sodium carbonate	5
Granular sodium fluoride	2
Granular trisodium phosphate ^a	1
Diesel oil (defoamer)	3

Pbw, part by weight.

^a Trisodium phosphate enhances the flame retardency.

and at different molding temperatures (80–160 °C) were tested for mechanical performance. The plastics were rigid and brittle having tensile strengths of 10–40 MPa, yield strengths of 1–5.9 MPa and elongations of 1.3–4.8%. Percent elongation increased and Young's modulus decreased with increase in water content of molding material. The yield strength was maximum (4.9 MPa) at a moisture level of 10.0%. The moisture uptake of the molded plastic specimens by immersion in distilled water at 25 °C for 26 h varied from 30 to 167%.

The plastic specimens from soy concentrate and soy isolate exhibited almost similar properties. An increase in molding temperature resulted in an increase in strength but reduction of extensibility. Plastics molded at 140 and 160 °C were strongest having yield strength of 49 MPa.

The morphology and mechanical behaviour of high protein content soy plastics prepared by compression molding at 150 °C and 19.6 MPa for 6 min was studied by Sue et al. (1997). A Young's modulus of 4.4 GPa could be obtained by keeping the moisture content below 5% (by weight). At the moisture content of 2.6% the soybean sheet had a very high tensile strength, but was brittle (Zhang et al., 1998). The maximum toughness was achieved at moisture content of 3.6%.

The high-fracture toughness observed in dry soy plastic was attributed to the formation of multiple arrays cavitated voids in the damage zone. The ductility and dimensional stability strongly depended on the moisture content. The glass transition temperature (T_g) of dry and moistened soy plastic was around 150 °C but upon addition of 25% (by weight) of glycerol as plasticizer, T_g reduced to –50 °C.

Soy plastics exhibited a shear storage modulus (G') of 1.76 GPa when moisture or other plasticizers (e.g. polyols) were absent (Wang et al., 1996). The storage modulus remained constant and was temperature insensitive up to 130 °C as revealed by dynamic mechanical spectroscopy (DMS). A significant decrease in shear storage modulus (0.22 GPa) was observed after ageing these plastics for 3 weeks at 50% relative humidity (RH). In DMS studies of soy sheets (containing glycerol and water) two transitions, one above 70 °C (soften-

ing of sheets) and another at sub-ambient temperatures, which may be due to glass transition (T_g) of the sheets, were observed by Zhang et al. (1998). The values of T_g depended on the moisture content and ranged from –71––35 °C (moisture range 26.0 and 2.6%). The relatively low T_g indicates the absence of cross-linking reaction during extrusion of soy protein sheets. The storage modulus in glassy region was higher in samples with higher moisture contents. This indicates anti-plasticisation effect of glycerol–water at extremely low temperature (Zhang et al., 1998).

For successful processing of soy protein, a similarity in the polarity of plasticizers to protein is important (Wang et al., 1996). Hence, water and polyols have been used as plasticizers in these formulations. The effect of structure of polyols on the mechanical properties of soy protein plastics has been reported by several workers (Wang et al., 1996, 1995; Zhang et al., 1998). Polyols such as propylene glycol, triethylene glycol, ethylene glycol, butane diols showed good compatibility with soy protein. Triethylene glycol seemed to produce the best tensile strength and percent elongation of soy protein plastics (Wang et al., 1996). Among all the plasticizers tested, ethylene glycol, glycerol and propylene glycol displayed the greatest effects on the percentage elongation at break of the plastic specimens. At 30% (w/w) concentration level, the plastic specimens containing ethylene glycol displayed about 400% elongation at break compared with those containing glycerol (330%) and propylene glycol (120%). This was attributed to small molecular weight and greater polarity of ethylene glycol. 1,3-Propane diol was less polar and less effective than those three (ethylene glycol, glycerol, propylene glycol) in changing the tensile properties of soy protein plastics. Poly(ethylene glycol) showed no significant effects on percentage elongation at break of the plastic specimen.

In addition to the effects of the polyhydric alcohols on the mechanical properties of the plastics, toxicity is another major concern for their application. Glycerol is non-toxic. Propylene glycol has very low order of toxicity but is more volatile (Monick, 1968). Ethylene glycol, however, is hazardous for food-related uses.

The DSC traces of commercial soy protein isolate did not exhibit the typical endothermic transition of 7S and 11S fraction (at 120 and 150 °C, respectively with 10% water content) indicating that commercial protein was denatured (Wang et al., 1996). Plastic performance of two major fractions of protein i.e. 7S and 11S was also studied (Sun et al., 1999b). It was found that plastics made from 11S-RG (rich globulins) at its thermal transition temperature were stronger and had lower water absorption than those made from 7S-RG at 145 °C. However, the plastics made from the mixture of 7S and 11S showed highest tensile strength and medium water absorption capacity. The molding temperature was varied from 120 to 175 °C. Tensile strength (MPa) and percent elongation (%) were maximum at 145 °C for 7S-RG and mixture of 7S-RG and 11S-RG plastics. However, 11S-RG showed maximum tensile strength and elongation at 162.5 °C. Thermal, mechanical and water absorption properties of SDS/guanidine hydrochloride (GH) modified soy protein (11S) (Zhong and Sun, 2001b) and blends of SPI with polycaprolactone (PCL) alone or in the presence of methylene diphenyl diisocyanate (MDI) have also been investigated by Zhong and Sun (2001a). DSC and DMA analysis showed that SDS or guanidine hydrochloride acts as a plasticiser for 11S and T_g decreased with increasing concentration of SDS or GH. Plastics made of 11S protein modified with 5% SDS had the highest tensile strength and % elongation. In case of blends, MDI acts as a compatibiliser and the mechanical properties of 50/50 SPI/PCL blends increased with increasing amounts of MDI. A significant improvement in water resistance was observed upon blending with polycaprolactone (PCL), which increased further upon addition of MDI compatibiliser (Zhong and Sun, 2001a,b, 2000).

Thermogravimetric analysis of molded soy protein plastics in nitrogen gas showed that plastics were stable up to 300 °C, indicating thereby good thermal stability. With the presence of oxygen, however, the plastics decomposed at 180 °C (Wang et al., 1995).

Biodegradation of molded soy protein in both the soil environment and in stimulated marine

environment showed a rapid conversion of plastics into carbon dioxide and water (Spence et al., 1996). The molded soy protein plastics degraded more quickly than the raw material. Soy protein/starch-blended plastics degraded very promptly. The differences in the degradation rates were attributed to the heat denaturation of protein and the balanced carbon and nitrogen sources in soy protein and starch blends. Soy protein plastic composite with enhanced stiffness, strength and water resistance have been obtained (Otaigbe and Adams, 1997a,b) using polyphosphate filler.

8. Applications

Soybean protein can be used to produce a wide variety of non-food products, including plastic films, building composites, insulating foams, plywood adhesives, and other wood bonding agents (Burnett, 1951; Were et al., 1997; Kuo et al., 1998; Krinski and CoCo, 1984; Wool et al., 2000b). A new product called 'Environ' has been introduced using 45% soybean flour, 45% recycled newspaper and 10% other ingredients (AG Innovation News, 1999). It has the appearance of granite and physical properties of wood. It has been used for interior applications such as table top, lamps etc. Biodegradable plastics have been obtained from SPI. Alternatively, SPI is used as additive to impart biodegradability to petroleum-based plastics (Salmoral et al., 2000; Mo et al., 2001). Soy protein provides excellent adhesion properties for paperboard industry and is easy to dispose after use. Secondly, it is not harmful for packaging food materials (Zhong and Sun, 2001a; Mo et al., 1999). Soy-phenol-resorcinol formaldehyde-based adhesives have been used for finger jointing green lumber and can be used for making composites using wheat straw or soy straw (agricultural waste).

9. Future prospects

Two main reasons for the interest in soy based industrial products are environmental friendliness and legislation. Mass media coverage of consumer

use and disposal of inert petroleum plastics, fuel consumption, waste oil disposal and other forms of water and air pollution have increased awareness about environmental issues and has forced the industries to look for eco-friendly materials based on soy bean and other naturally occurring renewable resources. Advances in genetic engineering, natural fibre development, novel composite material based on tenewable sources offer significant opportunities for development of improved materials based on soy protein in future.

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References

- AG Innovation News, 1999. vol. 8, No. 1.
- Bain, W.M., Circle, S.J., Olson, R.A., 1961. Synthetic and protein adhesives for paper coating, Technical Association of the Pulp and Paper industry (TAPPI). Monogr. Series 22, 206–241.
- Berk, Z., 1992. Technology of production of edible flours and protein products from soybeans. FAO Agric. Serv. Bull. 97, 1–10 Chapter 1.
- Bian, K., Sun, S., 1998. Adhesive performance of modified soy proteins polymers. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 39, 72–73.
- Bjorksten, J., 1951. Cross linkages in protein chemistry. In: *Advances in Protein Chemistry*, vol. 6. Academic Press, New York, pp. 353–358.
- Brandenburg, A.H., Weller, C.L., Testin, R.F., 1993. Edible films and coatings from soy proteins. *J. Food Sci.* 58, 1086–1089.
- Brown, O.E., 1987. Labelling adhesives. US Patent 4,675,351.
- Burnett, R.S., Eichenberger, W.R., 1948. Modification of soy protein for paper coating applications. *Paper Trade J.* 126, 51–52.
- Burnett, R.S., 1951. In: Markley, K.S. (Ed.), *Soybeans and Soybean Products*, vol. 2. Interscience Publishers, Inc, New York, pp. 1003–1053.
- Chae, H.J., In, M.J., Kim, M.H., 1997. Characteristic properties of enzymatically hydrolysed soy protein for use in protein supplements. *Han'guk Nonghwa Hakhoechi* 40, 404–408.
- Circle, S.J., Meyer, E.W., Whitney, R.W., 1964. Rheology of soy protein dispersions. Effect of heat and other factors on gelation. *Cereal Chem.* 41, 157–172.
- Clay, J.D., Vijayendran, B., Moon, J., 1999. Rheological study of soy protein-based PRF wood adhesives. *Annu. Tech. Conf. Soc. Plast. Eng.* 57th, vol. 1, pp. 1298–1301.
- Coco, C.E., Graham, P.M., Krinski, K.L., 1984. A protein adhesive binder. Eur. Patent 1,086,49.
- Coggeshall, B., 1999. *Int. Contrib. Wood Adhes. Res.*, [For. Prod. Soc. Annu. Meet.], Forest Products Society, Madison WI, pp. 129–131.
- Dykstra, G.M., Hollingsworth, R.L., 1975. Method for producing paper coating binder involving grafting unsaturated acrylate onto proteinaceous substrate in water. US Patent 3,920,592.
- Feeney, R.E., Whitaker, J.R., 1977. Food proteins: improvement through chemical and enzymatic modification. *Adv. Chem. Ser* 160, ACS, Washington DC, pp. 3–21.
- Feeney, R.E., Whitaker, J.R., 1985. In: Altschul, A.M., Wilcke, H.L. (Eds.), *Chemical and Enzymatic Modification of Plant Proteins in New Protein Foods*. Academic Press, New York, pp. 181–219.
- Franzen, K.L., Kinsella, J.E., 1976. Functional properties of succinylated and acetylated soy protein. *J. Agric. Food Chem.* 24, 788–795.
- Friedman, M., Liardon, R., 1985. Racemization kinetics of amino acid residues in alkali treated soybean proteins. *J. Agric. Food Chem.* 33, 666–672.
- German, J.B., O'Neil, T.E., Kinsella, J.E., 1985. Film forming and foaming behaviour of food proteins. *J. Am. Oil Chem. Soc.* 62, 1358–1366.
- Hamada, J.S., Marshall, W.E., 1989. Preparation and functional properties of enzymatically deamidated soy proteins. *J. Food Sci.* 54, 598–601.
- Hettiarachchy, N.S., Kalapathy, U., Meyer, D.J., 1995. Alkali modified soy protein with improved adhesive and hydrophobic properties. *J. Am. Oil Chem. Soc.* 72, 1461–1464.
- Hinterwaldner, R., 1997. Plant proteins as resources for innovation in backbone binders. *Coating* 30, 323–325.
- Hollow core flush doors, Report, 1983. U.S. Department of Agriculture Forest Products Laboratory, Madison WI (1954).
- Huang, W.N., Sun, X., 2000a. Adhesive properties of soy proteins modified by urea and guanidine hydrochloride. *J. Am. Oil Chem. Soc.* 77, 101–104.
- Huang, W., Sun, X., 2000b. Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecyl benzene sulfonate. *J. Am. Oil Chem. Soc.* 77, 705–708.
- Ignjatovic, N.L., Tomic, S.L.J., Vrhovacc, L.P., Miljkovic, J.P., Baras, J., 1998. Determination of optimal conditions for modification of urea formaldehyde adhesives by enzymatically modified soybean adhesive. *Hem. Ind.* 52, 286–289.
- Jane, J., Wang, S., 1996. Soy protein-based thermoplastic composition for preparing molded articles. US Patent 5,523,293.
- Johnson, O., 1923. Adhesive formula and the product produced. US Patent 1,460,757.

- Kalapathy, U., Hettiarachchy, N.S., Myers, D., Hanna, M.A., 1995. Alkali modification of soy protein and their adhesive properties on woods. *J. Am. Oil Chem. Soc.* 72, 507–510.
- Kalapathy, U., Hettiarachchy, N.S., Myers, D.J., Rhee, K.C., 1996. Alkali modification of soy proteins: effects of salts and disulfide bond cleavage on adhesion and viscosity. *J. Am. Oil Chem. Soc.* 73, 1063–1066.
- Kalapathy, U., Hettiarachchy, N.S., Rhee, K.C., 1997. Effect on drying methods on molecular properties and functionalities of disulfide bond cleaved by soy proteins. *J. Am. Oil Chem. Soc.* 74, 195–199.
- Karcher, L.P., 1997. The incorporation of corn and soybean based materials into plywood adhesives (soy molasses, phenolic resins). *Diss. Abstr. Int. B* 57, 7297.
- Kawamura, Y., Matsumura, Y., Matoba, T., Yonezawa, D., Kito, M., 1985. Selective reduction of interpolypeptide and intrapolypeptide disulfide bonds of wheat gluten from defatted flour. *Cereal Chem.* 62, 279–283.
- Kella, N.K.D., Kang, Y.J., Kinsella, J.E., 1998. Effect of oxidative sulfitolysis of disulfide bonds of bovine serum albumin on its structural properties. *J. Protein Chem.* 7, 535–548.
- Kim, S.H., Kinsella, J.E., 1986. Effects of reduction with dithiothreitol on some molecular properties of soy glycinin. *J. Agric. Food Chem.* 34, 623–627.
- Kinsella, J.E., 1979. Functional properties of soy proteins. *J. Am. Oil Chem. Soc.* 56, 242–258.
- Klemazewski, J.L., Kinsella, J.E., 1991. Sulfitolysis of whey proteins: effect on emulsion properties. *J. Agric. Food Chem.* 39, 1033–1036.
- Kowarsky, I., 1955. Methods for hardening proteins and the hardening solution. US Patent 2,722,484.
- Kriebich, R.E., 1995. New adhesives based on soy protein. *Oils-Fats-Lipids 1995, Proc. 21st World Congr. Int. Soc. Fat Res.*, 21st (1996) Meeting Date, vol. 3, P.J. Barnes & Associates, Bridgwater, UK, pp. 503–509.
- Krinski, T.L., CoCo, C.E., 1984. Use of soy polysaccharides as a thickening agent for alkali silicate adhesive. US Patent 4,437,893.
- Krinski, T.L., Hou, K.C., 2000. Vegetable protein-protein acrylate coprecipitate as binderthickener. Eur. Patent 1,054,103.
- Krinski, T.L., Scacciaferro, M.L., 1998. Protein adhesive binder and process for producing. Eur. Patent 083,851,3A2.
- Krinski, T.L., Steinmetz, A.L., 1987a. Protein modified with a silanation reagent as an adhesive binder and process of producing it. US Patent 4,713,116.
- Krinski, T.L., Coco, C.E., Steinmetz, A.L., 1987b. Cationic monomer-modified protein adhesive binder for paper coatings. US Ser. No. 696,941.
- Kuo, M., Adams, D., Myers, D., Curry, D., Heemstra, H., Smith, J.L., Bian, Y., 1998. Properties of wood/agricultural fibre cardboard bonded with soybean based adhesives. *For. Prod. J.* 48, 71–75.
- Lambuth, A.L., June 29, 1965. Process for the preparation of epoxide-modified adhesive compositions. US Patent 3,192,171.
- Lambuth, A.L., 1977. Soybean glues. In: Skeist, I. (Ed.), *Handbook of Adhesives*, 2nd ed. Van Nostrand, New York, pp. 172–180.
- Lambuth, A.L., 1994. Protein adhesives for wood. In: Pizzi, A., Mittal, K.L. (Eds.), *Advanced Wood Adhesive Technology*. Marcel Dekker Inc, New York, pp. 259–281.
- Lambuth, A.L., 2001. Blood and casein glues. In: Satas, D., Tracton, A.A. (Eds.), *Coatings Technology Handbook*. Marcel Dekker Inc, New York, pp. 519–530.
- Liang, F., Wang, Y., 1999. Effect of silane coupling agents on the interface of soy protein and glass fibre. *Proc. Am. Soc. Compos., Tech. Conf. 14th*, pp. 511–520.
- Lorenz, L.F., Conner, A.H., Christiansen, A.W., 1999. The effect of soy protein additions on the reactivity and formaldehyde emissions of urea formaldehyde adhesive resins. *For. Prod. J.* 49, 73–78.
- Mackay, C.D., 1998. Good adhesive bonding starts with surface preparation. *Adhes. Age* 41, 30–32.
- Market opportunity summary, February 2000. Soy-based wood adhesive.
- Mo, X., Sun, X.S., Wang, Y., 1999. Effect of molding temperature and pressure on properties of soy protein polymers. *J. Appl. Polym. Sci.* 73, 2595–2602.
- Mo, X., Hu, J., Sun, X.S., Ratto, J.A., 2001. Compression and tensile strength of lowdensity straw-protein particle board. *Ind. Crops Prod.* 14, 1–9.
- Monick, J.A., 1968. *Alcohols: Their Chemistry, Properties and Manufacture*. Reinhold, New York, p. 74.
- Myers, D.J., 1993. Industrial applications for soy protein and potential for increased utilisation. *Cereal Foods World* 38, 355–358.
- Otaigbe, U.J., Adams, O.D., 1997a. Novel bioabsorbable polyphosphate/soy protein plastic composites. *Int. SAMPE Tech. Conf.*, 29 (Composites for the Real World), pp. 686–697.
- Otaigbe, U.J., Adams, O.D., 1997b. Bioabsorbable soy protein plastic composites: effect of polyphosphate fillers on water absorption and mechanical properties. *J. Environ. Polym. Degrad.* 5, 199–208.
- Paetau, I., Chen, C.Z., Jane, J., 1994a. Biodegradable plastics made from soybean products. *Ind. Eng. Chem. Res.* 33, 1821–1827.
- Paetau, I., Chen, C.Z., Jane, J., 1994b. Biodegradable plastics made from soybean products. I. Effects of crosslinking and cellulose incorporation on mechanical properties and water absorption. *J. Environ. Polym. Degrad.* 2, 211–217.
- Paul, G.M., Krinski, T.L., 1983. Heat coagulable paper composition with a soy protein adhesive binder. US Patent 4,421,564.
- Petrucelli, S., Anon, M.C., 1995. Partial reduction of soy protein isolate disulfide bonds. *J. Agric. Food Chem.* 43, 2001–2006.
- Ph (Post harvest) Action News, 2001. Recent publication from FAO, No. 4.
- Rockville, M.D., 1982. Indirect food additives: paper and paperboard component; oxidised soy isolate. *Fed. Regist.* 47,51106.

- Sair, L., 1959. Soybean protein. US Patent 2,881,076.
- Salmoral, E.M., Gonzalez, M.E., Mariscal, M.P., Medina, I.F., 2000. Comparison of chickpea and soy protein isolate and whole flour as biodegradable plastics. *Ind. Crops Prod.* 11, 227–236.
- Schwalbe, H.C., 1961. Protein and synthetic adhesives for paper coating. Technical Association of the Pulp and Paper industry (TAPPI), Monogr. Series, 22.
- Seal, R., 1980. Industrial soy protein technology. In: Grant, R.A. (Ed.), *Applied Protein Chemistry*. Appl. Sci. Pub. Ltd, pp. 87–111.
- Shen, J.L., 1976. Solubility profile, intrinsic viscosity and optical rotational studies of acid precipitated soy protein and commercial soy isolate. *J. Agric. Food Chem.* 24, 784–788.
- Shih, F.F., 1994. Interaction of soy isolate with polysaccharide and its effect on film properties. *J. Am. Oil Chem. Soc.* 71, 1281–1285.
- Simmonds, D.H., Orth, B.A., 1973. Industrial uses of cereals. Pomeranz Amerc. Assoc. (Ed.), *Cereal Chem.*, St. Paul MN, pp. 51–120.
- Spence, K.E., Allen, A.L., Wang, S., Jane, J., 1996. *Am. Chem. Soc. Symp. Series* 627 (Hydrogels and biodegradable polymers for bioapplications), pp. 149–158.
- Steele, P.H., Kreibich, R.E., Steynberg, P.J., Hemingway, R.W., 1998. Finger jointing green southern yellow pine with a soy-based adhesives. *Adhes. Age* 41, 49–56.
- Steinmetz, A.L., Krinski, T.L., 1985. Modified protein adhesive binder. US Patent 4,554,337.
- Steinmetz, A.L., Krinski, T.L., 1987. Modified protein adhesive binder and process for producing it. US Patent 4,687,826.
- Stuchell, Y.M., Krochta, J.M., 1994. Enzymatic treatments and thermal effects on edible soy protein films. *J. Food Sci.* 59, 1332–1337.
- Sue, H.J., Wang, S., Jane, J.L., 1997. Morphology and mechanical behaviour of engineering soy plastics. *Polymer* 38, 5035–5040.
- Sun, X., Bian, K., 1999a. Shear strength and water resistance of modified soy protein adhesives. *J. Am. Oil Chem. Soc.* 76, 977–980.
- Sun, X.S., Kim, H.R., Mo, X.Q., 1999b. Plastic performance of soybean protein components. *J. Am. Oil Chem. Soc.* 76, 117–123.
- Tanford, C., 1968. Protein denaturation. In: Anfinsen, C.B., Anson, M.L., Edsall, J.T., Richards, F.M. (Eds.), *Advances in Protein Chemistry*. Academic Press, Inc. New York, pp. 121–283.
- Tarkow, H., 1979. In: Wangard, F.F. (Ed.), *Wood: Its Structure and Properties*. Materials Research Laboratory, Pennsylvania State University, University Park. 157 pp.
- Truax, T.R., 1929. The gluing of wood. *Bulletin* 1500. U.S. Department of Agriculture, Washington DC.
- Wang, S., Zhang, S., Jane, J.L., Sue, H.J., 1995. Effect of polyols on mechanical properties of soy protein. *Polym. Mater. Sci. Eng. (Am. Chem. Soc.)* 72, 88–89.
- Wang, S., Sue, H.J., Jane, J., 1996. Mechanical properties of soy protein plastics. *J. Macromol. Sci., Pure Appl. Chem. (Ed.)* A33, 557–569.
- Weakley, F.B., Carr, M.E., Mehlretter, C.L., 1972a. Dialdehyde starch in paper coatings containing soy flour-isolated soy protein adhesive. *Staerke* 24, 191–194.
- Weakley, F.B., Roth, W.B., Mehlretter, C.L., 1972b. Crosslinked protein glue containing chicken blood for interior-type plywood. *Hamm Douglas, Poult. Sci.* 51, 378–381.
- Were, L., Hettiarachchy, N.S., Kalapathy, U., 1997. Modified soy protein with improved adhesive and hydrophobic properties. *J. Food Sci.* 62, 821–823.
- Wildes, S.G., 20–21 June 2001. Industrial product utilisation of soybean derivative. Final Conference CTVO-net, Bonn (Germany).
- Wood Handbook: Wood as an Engineering, Material, Agriculture Handbook, vol. 72, U.S. Department of Agriculture, 1987. Forest Products Laboratory, Madison WI.
- Wool, R.P., Khot, S.N., LaScala, J.J., Bunker, S.P., Thielemans, W., Morye, S.S., 2000a. All natural composites for the transportation industry. *Polym. Mater. Sci. Eng. (Am. Chem. Soc.)* 83, 12.
- Wool, R.P., Khot, S.H., LaScala, J.J., Williams, G.I., Bunker, S.P., Morye, S.S., 2000b. In: Bandyopadhyay (Ed.), *Sustainable Composites from Renewable Resources*, Compos. Transp. Ind., Proc. ACUN-2: Int. Compos. Conf. 2, pp. 619–627.
- Wool, R.P., 1999. Development of affordable soy based plastics, resins and adhesives. *CHEMTECH* 29, 44–48.
- Wu, Y.V., Inglet, G.E., 1974. Denaturation of plant protein related to functionality and food applications. A review. *J. Food Sci.* 39, 218–225.
- Wu, W.U., Hettiarachchy, N.S., Qi, M., 1998. Hydrophobicity, solubility and emulsifying of soy protein peptides prepared by papain modification and ultrafiltration. *J. Am. Oil Chem. Soc.* 75, 845–850.
- Zhang, J., Mungara, P., Jane, J., 1998. Effect of plasticisation and crosslinking on properties of soy protein based plastics. *Polym. Reprints (Am. Chem. Soc. Div. Polym. Chem.)* 39, 162–163.
- Zhao, K., Hao, X.F., Liu, D.J., 2000. Soy protein isolate composite adhesive. *Zhengzhou Gongye Daxue Xuebao* 21, 15–18.
- Zhong, Z., Sun, X.S., 2000. Thermal and mechanical properties and water absorption of guanidine hydrochloride-modified soy protein (11S). *J. Appl. Polym. Sci.* 78, 1063–1070.
- Zhong, Z., Sun, X.S., 2001a. Properties of soy protein isolate/polycaprolactone blends compatibilised by methylene diphenyl diisocyanate. *Polymer* 42, 6961–6969.
- Zhong, Z.K., Sun, X.S., 2001b. Thermal and mechanical properties and water absorption of sodium dodecyl sulfate modified soy protein (11S). *J. Appl. Polym. Sci.* 81, 166–175.
- Zhong, Z., Sun, X.S., Fang, X., Ratto, J.A., 2001. Adhesion properties of soy protein with fibre cardboard. *J. Am. Oil Chem. Soc.* 78, 37–41.