5 Protein Adhesives

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5.1 I NTR ODUCTION

Nature uses a wide variety of chemicals for providing adhesion internally (e.g., cell to cell) and externally (e.g., mussels to ships and piers). This adhesive bonding is chemically and mechanically complex, involving a variety of proteins, carbohydrates, and other compounds.Consequently,the effect of protein structures on adhesive properties is only partially understood and creates an inherent difficulty in understanding protein structure-property relationships. This complexity has limited researchers in the past to mainly depend on empirical studies for insight, with a few exceptions.

For most protein adhesives, bonding of wood has not been a problem under dry use conditions, as the strength of the adhesives is sufficient to cause wood failure, but the adhesive bonds are weaker under wet-use conditions. Because of its economic importance, protein bonding has been widely studied the adhesion of mussels and barnacles to marine surfaces. The bioadhesion of organisms

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in marine environments is not covered here, because these proteins have not been used for formulating wood adhesives, but they have led to biomimicry and bioinspired research on modified and synthetic proteins that could be used as adhesives, as covered in Section 5.9.

Although nature has used proteins as adhesives for a wide variety of purposes, man-made protein adhesives have been used mainly for wood and paper bonding, because of the substrate's ability to transport the water solvent away from the bondline. Although protein adhesives have been greatly surpassed by synthetic adhesives for most bonding applications [I], wood bonding is one area in which there has been some increase in the use of protein adhesives in recent years [2]. Figure 5.1 shows the many types of wood products that have been made with protein adhesives. If sufficient wet cohesive strength can be developed, the adhesives can be used in an assortment of applications because of their ability to bond to a variety of wood species. However, the waterborne nature of protein adhesives has limited their use with most nonwood substrates.

Synthetic polymers have two main advantages over natural polymers. The first is that synthetic polymers can be designed to have specific properties, because the physical properties, functionality. and molecular weights can be controlled for peak adhesive performance. With natural polymers.

FIGURE 5.1 Wood products made with soy adhesives (except for the bottom product, made with a casein adhesive). From top to bottom: decorative plywood, hardboard, medium density fiberboard, particleboard, oriented strandboard, engineered wood flooring, and glulam.

utility can only be obtained from what nature has synthesized for another purpose, unless the biopolymers can be properly modified The second advantage is that synthetic materials can be made repeatedly with the same structural properties, whereas natural polymers have considerable variability in their properties.

The two main drivers leading to an increase in research on protein adhesives are the interest in materials made from natural sources and concerns about health hazards from the monomers used in synthetic wood adhesives. Wood is already a green material, but using natural polymer adhesives makes these products even greener. The health hazard concerns about synthetic polymers have been important because the most commonly used wood adhesive, urea-formaldehyde (UF), is made with formaldehyde, which is considered carcinogenic. UF adhesives can continue to release significant amounts of formaldehyde emissions of high heat and humidi5y ro4 5h3 lir3 or 5h3 product [3,5]. Formaldehyde emissions from products made with UF adhesives have been a concern for a long time [6,7]. The easiest to manufacture products are also those UF adhesives with the greatest strength. However, these products are made with higher formaldehyde-to-urea (F/U) ratios, which result in the highest formaldehyde emissions [5,8]. Thus, the trend has been to use lower F/U ratios, make changes to the synthesis conditions, and add scavengers to provide products with lower formaldehyde emissions [9]. The lower emission products are driven by new regulations, companies' desires to be green, or concern about long-term legal liability for producing products with higher formaldehyde emissions [10-13]. Although some applications allow higher formaldehyde emissions, the trend has been to lower the formaldehyde emissions to the level that naturally occurs in wood. Processing can increase the formaldehyde emissions of some wood products, requiring adhesives that can absorb this formaldehyde and are free of added formaldehyde [14]. The desire for formaldehyde-free adhesives has been an important driver for the resurgence of soy adhesives, because they retain low emissions levels even under high temperature and humidity conditions [4]. The problem concerning formaldehyde emissions resides solely with UF adhesives, since the phenol-, resorcinol-, and melamine-formaldehyde adhesives generally do not have formaldehyde emission issues.

Although the emphasis has been on emissions from the final wood product as used by the customer. there are also concerns about hazardous emissions during the production processes for adhesives and bonded wood products [14.15]. Given that adhesives generally need to react to form the adhesive bond, there is always a concern that adhesives may react with human proteins, nucleic acids, and so forth impacting worker health. Certainly, this has been an issue with some of the formaldehyde-containing adhesives. Concern surrounding isocyanate adhesive use in wood bonding processes has also been raised [16]. Generally, wood adhesives ha e the advantage of being waterborne; thus, they normally have a low amount of volatile organic compounds relative to solvent-borne adhesives. Although workplace exposure to the adhesives can be minimized by good manufacturing practices, some facilities do not even consider using isocyanate adhesives for fear of worker exposure.

Many market forces, including the facts of being biobased, being potentially free of added formaldehyde, and having better recyclability, favor proteins as wood adhesives if they can provide sufficient product performance. The most available source of proteins is plants, primarily seed crops. These plants are separate into oil seeds (harvested mainly for their oil) and cereal grains (harvested mainly for their carbohydrate content). Table 5.1 shows the approximate compositions of a variety of seed materials. The soybean is clearly the best source, given the high protein content compared with other oil seeds, and soybeans are much higher in protein than cereal grains. Even though the high-value human food market is the driving force behind the growing and processing of these crops, industrial chemicals provide valuable outlets for portions of these products that are often used as amimal (cattle and pig) feeds. Finding additional value for the by-products can improve the overall economics of growing and processing these plants. This was especially true in the past for many industries that converted waste materials into valuable adhesives, especially in animal and plant processing. Collagen from cattle and horse hooves and hides and fish skins was important for glues in the paper and furniture industries. Additionally, blood glues from pigs and cattle were important for the wood bonding industry. The use of proteins in pet foods, gardening aids, and other high-value products has led to

TABLE 5.1
Comparison of Protein Contents and Other Compounds in Compositions of Various Oilseeds and Cereal Grains in Weight Percentages (Average Data Taken from a Number of Sources)

Source	Protein	Fat	Starch	Fiber	Ash
Oil Seeds, Harvested Primarily for Oils					
Soybean	51	20	0	6	6
Rapeseed	26	46	0	5	8
Canola	22	41	22	10	5
Cottonseed	22	20	35	19	5
Linseed	24	43	29	8	3
Peanuts	30	50	14	3	3
Safflower	21	41	15	19	5
Sunflower	21	55	18	2	3
Cereal Grains, Harvested Primarily for Carbohydrates					
Wheat	12	2	72	2	2
Corn/maize	10	5	80	2	1
Oats	11	6	56	11	3
Rice	8	1	76	1	1
Rye	12	2	72	2	2

Source: Lusas, E.W., Oilseeds and oil-bearing materials, in: Handbook of Cereal Science and Technology, K. Kulp and G. Points, Jr. (Eds.), pp. 297-362, Marcel Dekker, New York, 2000; Salunkhe, D. K. et al., *World Oilseed Chemistry, Technology and Utilization*, Van Nostrand Reinhold, New York, 1991; Wolf, W. J., Soybeans and Other oilseeds, in: Kirk-Othmer Encyclopedia of Chemical Technology. 3rd eds, Vol. 21, pp. 417-442, Wiley New York, 1983; Lasztity, R., *Chemistry of Cereal Proteins*, CRC Press, Boca Raton, FL., 1995. Modified from X.S. Sun. Overview of plant polymers: Resources, demands, and sustainability. In: *Bio-Based Polymers and Composites*, R. P. Wool and X.S. Sun (Eds.), pp. 1-14, Elsevier-Academic Press, Burlington, MA, 2005

the near extinction of most protein adhesives. Although animal-derived protein adhesives are less important, some of the plant materials are more likely to be used as adhesives in the future.

To think effectively about the adhesive performance of proteins, it is important to understand The structure-property relationships of proteins. This is very important, because proteins are very different in structure from most polymers, especially synthetic polymers, and thus have very different in structure-property relationships. In this chapter, after an overview of protein structure, protein adhesives from specific sources are discussed. Unfortunately, because of the wide variety of proteins properties, there is no real way with current knowledge to relate performance characteristics with specific structural elements for these proteins in normal plant products. Hydrophobic and polar interactions, colloidal properties, and the aggregation state of the protein are important parameters that influence adhesive properties. Protein colloidal properties are influenced by the hydrophilic and hydrophilic properties of the surface and the ionic charge of the protein [21]. Thus, an understanding of the hydrophobic properties of the protein is important, as well as distribution of the polar groups in the protein. The aggregation of the protein, through both hydrophobic and hydrophilic attractions, suggests that the native protein properties are a summation of a number of individual protein chains of different compositions and structures [22]. These specific native quaternary aggregates often exist even if some of the individual proteins have denatured secondary structures [22,23].Developing an understanding of the properties of these protein aggregates is important, with much of the information corning from studies for food applications [24]. This information is an important addition to the adhesive literature in understanding protein rheological and strength properties, especially for the properties in the wet state, but it provides less information about dry and rewetted state properties.

Proteins are important contributors to the texture properties of food, which depend on both the chemical and physical properties of the proteins as they interact with other food ingredients. Food proteins are characterized by their solubility, viscosity, water binding, gelation, cohesion-adhesion, elasticily, emulsification, foaming, and fat and flavor bonding [21]. Many of the proteins' properties are relared to their surface tension; this is commonly determined by measuring the ease of aqueous foam formation and its stability, and by the gelation properties. The good surfactant behavior of proteins suggests that they should be good adhesives for wetting bonding surfaces. Gelation, cohesion, and elasticity are dependent on gel formation properties, which are measured by indentation tests after heating aqueous dispersions followed by cooling them to form a gel. These properties would, hopefully, carry over to their cohesive strength properties as adhesives.

Because the protein adhesive formulations widely used in the past are not used much nowadays, only a brief coverage of these adhesive formulations is provided and references are made to the best literature sources for more detailed application information. More importantly, this chapter contains information on protein structures and their related chemical and physical properties, which influence current and future applications of proteins as adhesives. The amino acid composition of each type of protein is given, but the literature data are for a single sample and do not reflect the natural variability in composition. Yet, understanding the compositions can assist in developing specific modifications or coreactants for future research work, such as providing information on the amount of side-chain functional groups potentially available for modification. However, because of the folding of the protein, many of these functional groups are not available for reaction if they are buried inside the protein.

5.2 PROTEIN STRUCTURE

It is difficult to make sense of a protein's properties without understanding its structural complexity involving specific hierarchical orders. The protein chain is composed of 21 naturally occurring amino acids. The amino acids are linked in a linear fashion through condensation reactions between the amino and carboxylic acid groups. The protein's backbone imposes some restrictions on the chain flexibility, especially in the case of the proline and hydroxyproline amino acids, which cause a pronounced kink in the chain because of their cyclical structure. The side chains impose additional restrictions on chain conformations. The sequence of the amino acids in the protein chain is called the *primary structure* [21,22]. Sometimes, a change in sequence can alter the protein's function, especially in enzymes, and other times it may not, such as in storage proteins. For a particular plant protein, amino acid composition has some minor natural variation in its composition caused by plant and growth condition diversity.

As shown in Figure 5.2, the different amino acids are either aliphatic, aromatic, or heterocyclic with many types of functional groups. Thus, a wide variety of interactions are possible between the hydrophobic and hydrophilic (acidic, basic, hydroxyl, and thiol) side groups on the amino acids. Different proteins vary in the percentages of amino acids and in amino acid sequences. Given that typical proteins are more than 200 amino acids long and each amino acid is selected from one of the 21 amino acids, this means that there can be a huge number of protein sequences.

The primary sequence of amino acids determines the secondary structure, which in turn, influences the tertiary structure of a protein and the protein's physicochemical properties. Certain sequences of amino acids can lead to either a-helix or b-sheet structures, which are called the *secondary structures* [22]. These secondary structures form as the protein is being synthesized, and are important for developing the native structure of the protein because they control the folding of the protein. These structures are intrachain elements and can be disrupted by heat and various chemical additives. They should not be confused with the interchain helix formed by collagen proteins and the interchain sheet crystallites that form in synthetic polymers [25].

Most proteins, including those used in adhesives, are globular proteins that have enough hydrophobic portions or weakly hydrophilic portions to cause the protein to fold inward in an aqueous

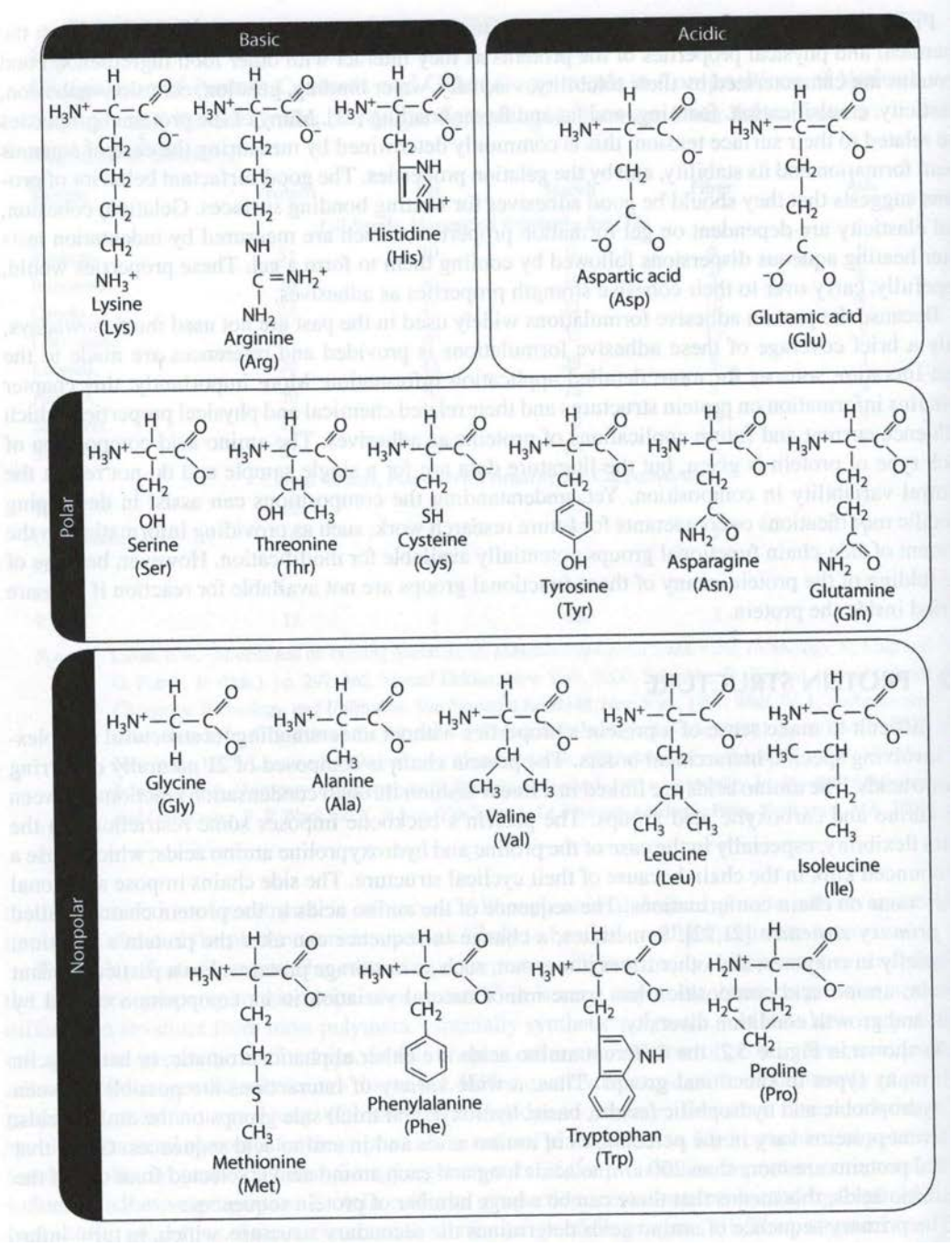

FIGURE 5.2 Common amino acids functional groups.

environment (Figure 5.3). During this hydrophobic collapse. intramolecular association of hydrophobic amino acids moves them mainly to the inside of the globular structure and the Polar amino acids preferentially to the outside. However. the primary and secondary structures limit the ability of partocular aminoacids to move to these separate regions. The polar groups on the inside of the globule are stabilized by associating with other polar groups on the chain. These types of interactions include not only hydrogen bonds, but also acid-base salt bridges and disulfides from the third

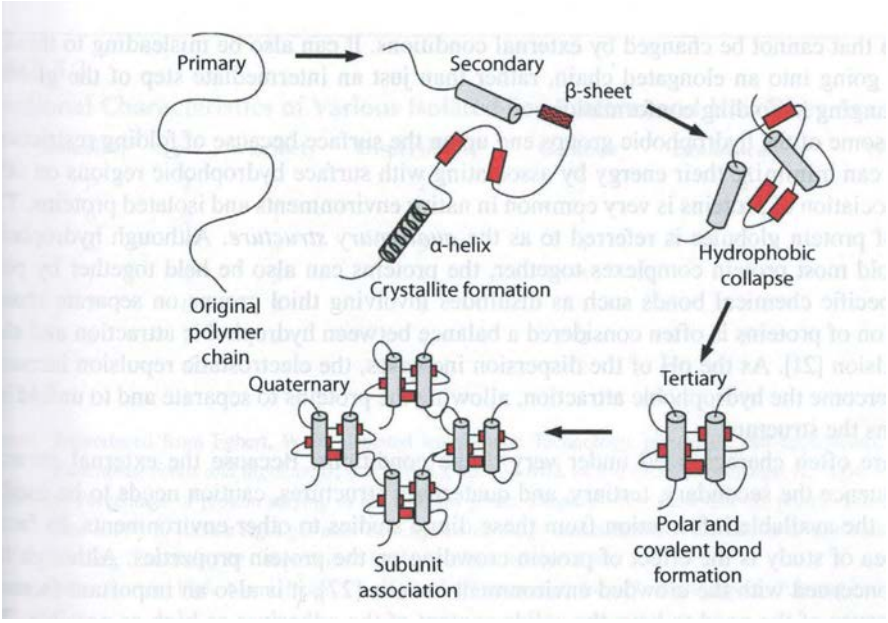

FIGURE 5.3 Protein folding as discrete steps for illustration purposes. In reality, the primary, secondary, and tertiary structures occur mainly at the same time.

groups. Some of the hydrophobic amino acids end up on the outside of the structure. This folding of the protein is refered to as its *tertiary structure.*

As the protein is being synthesized, the secondary and tertiary structures form to provide the native state of the protein. This native state is only a localized energy minimum, and thus, the native state may not be the most stable state [23, 26]. As shown in Figure 5.4, there are many energy minimums (B, C, etc.) in addition to the native state (A) that may not be very different in energy from the native state, although there are some larger troughs for particular conformations. The small activation energies mean that the protein can readily change its conformation depending on the external environment. The similar energy minimums represent changes that may occur in the protein colloid with changes in the electrical double layer with alterations of the aqueous environment, such as the addition of salts, urea, or other chemicals. The larger activation energy maximums and deeper troughs represent the unfolding and refolding of the protein chain within the protein globule during thermal denaturation of the proteins. Thus, it can be very misleading to assume that there is a single

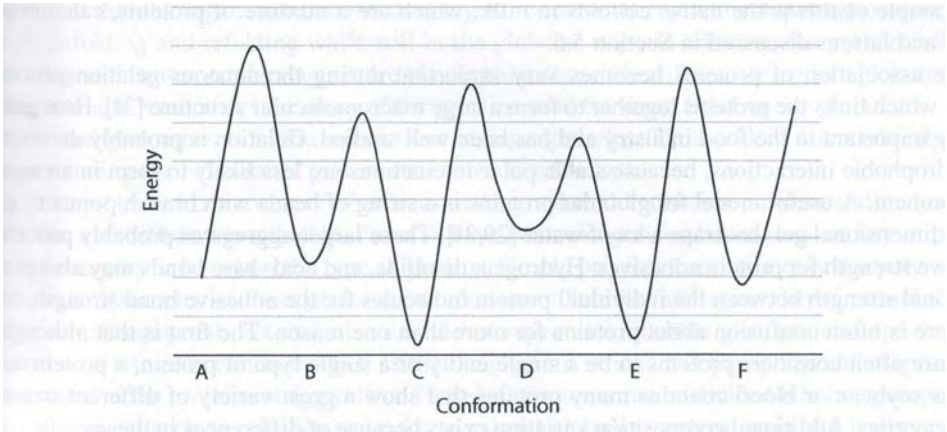

FIGURE 5.4 Typical protein energy versus conformation, where differences are a few calories per mole between the native state A and denatured states B, C, and so forth.

conformation that cannot be changed by external conditions. It can also be misleading to think of unfolding as going into an elongated chain, rather than just an intermediate step of the globular protein in changing its folding conformation.

Although some of the hydrophobic groups end up on the surface because of folding restrictions. these groups can minimize their energy by associating with surface hydrophobic regions on other proteins. Association of proteins is very common in native environments and isolated proteins. This association of protein globules is referred to as the *quaternary structure.* Although hydrophobic attractions hold most protein complexes together, the proteins can also be held together by polar bonds and specific chemical bonds such as disulfide involving thiol groups on separate chains. The association of proteins is often considered a balance between hydrophobic attraction and electrostatic repulsion [21]. As the pH of the dispersion increases, the electrostatic repulsion increases enough to overcome the hydrophobic attraction, allowing the proteins to separate and to unfold in a way that opens the structure.

Proteins are often characterized under very dilute conditions. Because the external environment can influence the secondary, tertiary, and quaternary structures, caution needs to be used in extrapolating the available information from these dilute studies to other environments. In fact. a prominent area of study is the effect of protein crowding on the protein properties. Although this research is concerned with the crowded environment in cells [27], it is also an important factor in adhesives because of the need to have the solids content of the adhesives as high as possible. The crowding can significantly impact protein-protein and protein-carbohydrate interactions compared with the characterization of proteins under very dilute conditions.

Given the complex structural nature of proteins, when discussing adhesive performance, the history of the protein in prior processing needs to be understood. It is also important to remember the most natural sources contain many different proteins and, in many cases, the proteins are intimately associated with other materials, such as carbohydrates, which can influence their properties. The natural state of the protein is called the *native state,* which is a singular structure for each protein, and any transformation from the native state is called a *denatured state.* Obviously, there are many denatured states, whereas there is only one native state. Some disruptions can be measures to understand what has happened, such as the loss of secondary structure, but detailed changes in the tertiary structure are hard to determine. Many methods have been developed to measure the properties of proteins [28].

Although the discussion of proteins ends at times at the quaternary structure, there are often higher-order structures of a macromolecular nature. These can be due to larger protein agglomerates [29], or they can also be proteins associating with carbohydrates [30]. In fact, after synthesis of the amino acid backbone, proteins can be modified by attachment of carbohydrates or phosphates. An example of this is the native colloids in milk, which are a mixture of proteins, calcium phosphate, and fats, as discussed in Section 5.5.

The association of proteins becomes very important during the aqueous gelation process in water, which links the proteins together to form a large macromolecular structure [31]. Heat gelatin is very important in the food industry and has been well studied Gelation is probably driven me by hydrophobic interactions, because stable polar interactions are less likely to form in an aqueous environment. A useful model for globular proteins is a string of beads with branch points to give a three-dimensional gel that traps a lot of water [29,311. These larger aggregates probably provide the cohesive strength for protein adhesives. Hydrogen, disulfide, and acid-base bonds may also provide additional strength between the individual protein molecules for the adhesive bond strength.

There is often confusion about proteins for more than one reason. The first is that although the literature often considers proteins to be a single entity or a single type of protein, a protein source such as soybean or blood contains many proteins that show a great variety of different structure and properties. Additional composition variation exists because of differences in the specific source and processing of the proteins. The processing can influence the proteins' bonding properties, as illustrated by the differences in chemical and physical properties, which are shown in Table 5.2 for

TABLE 5.2

Functional Characteristics of Various Isolated Soy Proteins and How They Are Rated

Soy	Solubility*	pH	Viscosity	Dispersibility*	Gelation*	Emulsification*	Water Binding
A	7[a]	7	7	2	7	6	7
B	6	6	1	3	1	7	1
C	4	5	4	5	4	3	4
D	7	7	5	4	5	6	6
E	7	6	3	1	3	7	3
F	2	3	2	6	2	2	2
G	7	6	2	3	2	7	2
H	1	1	1	7	1	1	1

Source: Reproduced from Egbert, W. R., Isolated soy protein: Technology, properties, and applications, in *Soybeans as Functional Foods and Ingredients,* K Liu (Ed.), pp. 134162, AOCS Press, Champaign, IL, 2004. With permission

**Solubility:* Percentage of protein staying in the aqueous phase; Dispersibility: How fast the protein solubilities Gelation The ability to form a rigid gel after heating and cooling; Emulsification: The ability to mix water and fat; Water binding: The ability of the protein to hold water in a food product

[a]*Rating system:* 7=very high, 4 =moderate. I=very low. pH range reportedas 7=high(approx. 7.5)and I =low (approx. 4.5),

different soy protein isolates [32]. The second reason is that there are very few isolated proteins found in natural products; proteins are typically found as structures containing different amino acid sequences. In native form, these complexes are usually characterized, but once proteins have been denatured, the variety of structures present grows dramatically. Thus, a researcher needs to be in making generalized claims about a specific protein being a good adhesive. The importance of understanding the source and processing of proteins in ascribing mechanisms to adhesive performance cannot be overstated

There are also several other issues with proteins that can lead to confusion. The terms *solubility* and *dispersibility* are used for commercial products. Most proteins are not truly soluble, because of their high molecular weight and low polarity; thus, proteins are dispersions in water. The term dispersibility refers to how quickly the protein solids are welted when brought into contact with water, whereas solubility refers to how much of the protein stays dispersed after mechanical agitation the protein-water mixture is stopped The term *unfoldedprotein* is often used to describe changes in the protein. " Unfolded" does not mean that the protein goes into an extended polymer structure in water, but that the organized areas in the polymer become disrupted by denaturation conditions through unfolding and refolding while still in the globular state. In addition, the protein is altered by swelling with water, conferring a more plastic behavior while still remaining in a globular state. it is important to remember that many of the proteins used for wood bonding are globular in nature and their strength comes from the interactions of these globules. Thus, colloid science is important in understanding the behavior of protein structures as adhesives.

Because proteins from a variety of sources make good wood adhesives, understanding how the are similar and different is valuable. Proteins have been categorized based on a variety of properties. One category is based on the type of protein. Simple proteins consist of only the polymerized amino acids. Examples of these proteins include some albumins, collagens, keratins, and the glycinin in soy. Conjugated proteins, also called *heteroproteins,* include glycoproteins (protein plus carbohydrates are quite common, such as the conglycinin in soy) and phosphoproteins (phosphate groups added to the proteins in egg yolk and caseins). Proteins can be divided intotwo groups based on shape: fibrous (such as collagen and a-keratins) and globular (such as grain and legume storage protiens). Another major differentiation of proteins is albumins, which dissolve in water but not in salt solutions, compared with globulins, which dissolve in salt solutions.

5.3 SOYBEAN

Soybeans were historically, and are again, the dominant source of industrial protein adhesives, and have been used for commercial bonded wood products. Soy proteins are mainly storage proteins used to provide the growing plant with nutrients. Although many other protein adhesives were used long before soybeans, most are fairly expensive or limited in quantity. Soy proteins appeared to be a good replacement for the other proteins given cost and availability, but considerable effort was needed to develop soybean flour into a useful adhesive for wood bonding [33]. Although soy flour adhesives did not achieve the same degree of moisture resistance as some other proteins, such as casein and blood, they were suitable for interior plywood, leading to a significant expansion of that industry [1,34]. Soy protein's recent return to the wood bonding market has been almost exclusively in interior products, with the aid of coreactant components in the adhesive formulation to enhance water resistance.

Since a number of soy protein products are available, it is important to understand how each one is derived, because the processing affects the physical and chemical properties of the protein. After the soybeans have been dried and solvent-extracted to remove the valuable oil, the solvent is removed and the soybeans are ground to produce flour [35]. Soybean Hour is relatively inexpensive, available in very large quantities without disrupting the human food supply, and fairly consistent in composition. It contains about equal amounts of protein and carbohydrates, along with lipids and salts. The carbohydrates are about half soluble, consisting mainly of sucrose, raffinose, and stachyose, and half insoluble, consisting of rhamnose, arabinose, galactose, glucose, xylose, and mannose polymers [36]. The protein components have many types of functionalized side chains (Figure 5.2). The individual soy proteins are globular and readily form aggregates that constitute the 7S (β- conglycinin) and 11S (glycerin) fractions, with conglycinin plus glycerin making up about 80% of the total protein content of the Hour. A 2S fraction consists of low molecular mass polypeptides in the range of 8-20 kDa and is mainly the soybean trypsin inhibitors [37,38]. The 15S protein is probably a dimer of glycerin. As the data shown in Table 5.3, there are considerable differences in composition between the conglycinin and glycerin. As with most vegetable proteins, the weight percentages of aspartate plus aspartic acid, and glutamate plus glutamic acid, are large for both proteins, but the conglycinin has more arginine and lysine than the glycerin. The glycinxn is a dodecamer with two coplanar rings of protein with a molecular mass of 300-380 kDa, with each ring composed of three acidic polypeptides, each with a molecular mass of about 35 kDa, and three basic polypeptides, each with a molecular mass of ≈ 20 kpa. The acidic and basic polypeptides are linked together by a single disulfide bond in addition to the ionic attraction. The β- conglycinin is a turmeric glycoprotein with a molecular mass of 150-200 kpa, and consists of three types of subunits: α' (72 kDa,) α (68 kDa,) and β (52 kDa.) Information is provided here in compact form, and the reader is referred to the following references for additional information on soy protein structure [31,37,39-41].

It is natural to expect that with all these reactive moieties in the soy proteins (Table 5.3), it would be easy to develop covalent bonds of the protein subunits and agglomerates with cross-linkers. However, many of these reactive groups are not exposed on the surface, but are buried inside the globule, making reactions difficult. Furthermore, the polar groups inside the protein form interactions with other polar groups to stabilize the protein structure, making reactions even more difficult with these polar side chains.

Of all the commercial protein adhesives, those using soy Hour are the only ones with a high carbohydrate:protein ratio. Commercially, the Hour comes in three varieties, based on the protein permissibility index (PDI), with 90 PDI having the lowest level of thermal treatment and the highest amounts of the native proteins and 70 and 20 PDI having increasing levels of thermal treatment and increased amounts of denatured proteins. The PDI is the percentage of protein (as determined by nitrogen content) in the flour that can form a stable dispersion in water. The flour can be further

TABLE 5.3
Amino Acid Contents in Weight Percentage for Soy Protein, Soy Glycinin, and Soy Conglycinin

Amino Acid	Soy Protein	Soy Glycinin (11S)	Soy Conglycinin (7S)
Alanine	6.0	5.2	3.7
Arginine	4.7	5.8	8.8
Aspartate+ aspartic acid	16.9	20.0	20.5
Cysteine	1.0	1.4	0
Glutamate+glutamic acid	11.6	11.9	14.1
Glycine	9.7	7.5	2.9
Histidine	5.0	1.9	1.3
Isoleucine	2.9	4.2	6.4
Leucine	8.0	7.0	10.3
Lysine	5.9	4.4	7.0
Methionine	1.2	1.0	0.3
Phenylalanine	3.9	3.8	7.4
Praline	5.7	6.9	4.3
Serine	7.5	6.7	6.8
Threonine	4.0	3.9	2.8
Tryptophan	NA[a]	0.8	0.3
Tyrosine	2.6	2.8	3.6
Valine	3.4	4.8	5.1

Source. Sun, X. S., Isolation and processing of plant materials, in: *Bio-Based Polymers and Composites,* R P. Wool and X. S. Sun (Eds.), pp. 33-55, Elsevier-Academic Press, Burlington, MA, 2005.

[a]*NA:* not available.

processed by removal of the soluble carbohydrates to form a protein concentrate or by removal of both soluble and insoluble carbohydrates to yield a protein isolate.

There are several ways to make soy protein concentrate, but they all involve the denaturation of proteins to decrease their solubility to allow soluble carbohydrates to be separated from the protein. The most common method uses an aqueous ethanol extraction of the soluble carbohydrates and some low molecular weight proteins, and involves an ethanol denaturation and insolubilization of the main proteins [42]. Concentrates can have different properties, because some are produced directly from the extraction process, whereas others go through a jet cooking process that involves a short, high-temperature treatment of the aqueous soy, followed by rapid cooling Jet cooking is often called *functionalization,* because the soy functions better in food applications. This jet cooking greatly alters the protein, although the altered structure is not well understood [32]. It is important to understand the processing history used to make the concentrate, because processing history can dramatically alter the properties of soy concentrate and complicate the interpretation of the data. Because of the alteration of the protein in the extraction process, concentrates cannot be simply viewed as the soy flour with the soluble carbohydrates removed.

The purest commercial soy protein available is the isolate, which is produced by dissolving the native soy flour in water to allow the insoluble carbohydrates to be removed by centrifugation, followed by precipitation of the proteins by acidification to the isoelectric point and centrifugation. This process is used to prepare the native soy protein isolate (SPI) [35]. However commercial SPI is far different from the conditions and equipment used to prepare the isolate in the laboratory, and is intentionally altered to improve its functionality in food applications. These functionalized proteins are produced through jet cooking and sometimes by enzyme treatments [32]. Although native SPI

has the same differential scanning calorimetric glass transition peaks as those in native flour, and water dispersion is relatively low in viscosity, neither of these is true of commercial SPIs. In addition, commercial SPI is orders of magnitude better in providing wood bonds with good wet strength than the laboratory SPI [2]. Thus, the use of commercial SPI as a model for protein in soy Hour is often technically quite misleading

5.3.1 High-pH Soy Flour Adhesives

Although plywood was developed using other adhesives, such as animal protein, it gained commercial significance using soy flour with high pH (>12) conditions [1,33,34,43]. Much of the literature emphasizes the use of basic conditions with sodium salts for solubility and calcium salts for water resistance. In the current theories of proteins, basic conditions cause the polymer chains to be separated and somewhat uncoiled, because of the electrostatic repulsion overcoming the hydrophobic attraction. This can certainly be true for monovalent cations, but divalent calcium cations should hold the proteins together better. One report indicated that commercial formulations were more complicated, including the use of carbon disulfide [331.These adhesives were the main adhesives for interior plywood until UF adhesives took over the market in the 1940s and 1950s. As with any new adhesive, UF formulations and curing conditions needed to be optimized to produce a consisted product. The transfer to UF required several changes from the high-pH soy adhesives, including th use of hot presses to replace the cold presses used with soy. Another change for safety and economic reasons required the UF adhesive to be made in a supplier's factory and shipped to the plywood plant, where the curing catalyst and filler were added just prior to application of the adhesive. The soy adhesives had been made in the plywood plant and, thus, the formulation could be modified for changes in wood furnish and plant conditions, such as temperature and humidity.

Another commercial application of soy adhesives was in finger-jointed studs using a honeymoon adhesive with soy hydrolysate applied to one wood surface and a phenol-resorcinol-formaldehyde (PRF) to the other wood surface [44,451. This allowed successful finger jointing of green (undried) pieces to form nominal 2 x 4 in. (actually 38 x 89 mm [1.5 x 3.5 in.] after drying) studs [46]. This process was developed to use an environmentally friendly soy adhesive that substantially decreased adhesive costs by decreasing the amount of PRF needed and cut processing costs by not having to dry the wood first.

Given that the soy adhesives were manufactured under basic conditions, as are phenol-formaldehyde (PF) adhesives, it occurred to some researchers to combine soy with PF to decrease the cost [47-52]. However, a significant problem was that the soy formulations were much more viscous in combined adhesives compared with the PF alone. Two ways to address this problem were to keep the amount of soy low or to hydrolyze the soy flour to decrease its molecular weight However, neither of these methods was useful, because they did not allow incorporation of much soy flour into the PF adhesive. Later research showed that the high viscosity was not as much of a problem as had been previously thought, because the protein dispersions are shear thinning. Thus, although high viscosity for a regular PF would lead to application problems, because it is nearly Newtonian in viscosity, a high-viscosity soy adhesive worked under the high shear conditions involved with most application equipment. Thus, it is not necessary to match the viscosity of a phenolic resin with that of a soy adhesive. With this approach, up to 50% soy can be used in an adhesive resin that is useful as an oriented strand board (OSB) face resin. An interesting discovery was that the pH of an alkaline soy-PF adhesive could be lowered to a neutral pH to make soy-PF dispersion that is both a light-colored, low-viscosity adhesive and one that provides good bond strength [53]. Normally, PF resole adhesives are dark colored and need to be kept at high pH to prevent precipitation, unless a surfactant is used. Most proteins are surface-active agents, and this property is widely used in the food and other industries but has not been used much in the chemical industry. Although soy can be used as a substitute for a large portion of the PF, this process has not been commercialized

5.3.2 MODERATE-PH S0Y FLOUR ADHESIVES

In the previous section, we covered adhesives made using soy Hour with pH values of 12 or higher to denature the soy protein. This section discusses soy adhesives made using pH values of 6-10.

Lower pH values had not been used, because they approach the isoelectric point of the proteins (pH 4-6 depending on the protein), which causes the protein to become more compact and precipitate. A pH below the isoelectric point is not in a useful range for a wood adhesive, because wood degrades with time at low pH values (<3). Soy protein with a wide variety of functional groups can react with a number of other chemicals [2,60]. For example, soy protein can react with formaldehyde and other aldehydes, mainly under more basic conditions, but this depends on the aldehyde. At a lower pH <7, the reaction products are often weak gels. Most of the studies on the higher pH systems above 12 were for adhesives used in lamination, such as plywood, but a number of investigations have also involved binder applications [60].

The discovery of polyamidoamine-epichlorohydrin (PAE) resin as a co reactant with soy by Li and others [54,55] led to a successful line of commercial Soyad adhesives by Solenis of Wilmington, DE (previously by Ashland and Hercules) for interior wood products, with a pH between 5 and 9 [56]. The concept is that PAE can react with both soy and wood, forming a bridge between wood surfaces. Although the original disclosure was with commercial SPI, the reaction with PAE also works well with soy Hour. This technology was welcomed commercially, because it is a no-added formaldehyde (NAF) interior adhesive, and the California Air Resources Board (CARB) has decreased formaldehyde emissions from interior wood products in response to formaldehyde being declared a carcinogen. Columbia Forest Products (Greensboro, NC) wanted all their interior plywood to be NAF and developed the PureBond product line. Although soy with PAE is a major adhesive in this application in the United States, ultralow-formaldehyde-emitting UF is still a major player in the world market. These soy adhesives are also used for engineered wood flooring and particleboard

Another soy technology that has been used commercially involves soy and magnesium oxides, in which the soy probably serves as a binder for the oxide and wood [57,581. This technology has successfully worked in plywood plants. Both soy flour and SPI have been used as binders, along with other additives in this type of product.

Numerous other ways to modify soy proteins for adhesive applications are not reviewed here, because good reviews have been published [2,41,59,60]. Only very limited studies exist in the literature on these processes, and to our knowledge none were examined commercially. Sun has reviewed research on modifying native SPI showing that urea and surfactant addition can improve bond strength [59]. Sun has also reviewed aspects of soy structure and different ways to modify soy for adhesive applications [37,41]. VnuCec and others have carried out a more thorough review of soy protein modification for soy adhesives [60]. Frihart and Birkeland have addressed the problem of comparing different soy products for wood bonding [2]. The major problem in assessing these studies is that bonding is often done with each study using its own wood species and only one bonding condition. With the large effects of soy type, wood species, bonding temperature, rheology, and type of strength test, relating the strength tests from different studies is tenuous.

5.4 OTHER PLANT PROTEINS (WHEAT GLUTEN, RAPESEED/ CANOLA, LUPINE, COTTONSEED)

Other plant proteins have not been as widely explored as soy or used commercially in the past, probabl because of limited availability and cost. However, because of the tremendous advances in urn of plant materials grown per acre through genetic selection and engineering, fertiliza-
-- irrigation, and mechanical improvements at all stages of plant production, plant protein
, me by far the least expensive protein source. Although soybeans are an inexpensive plant
- the United States, Argentina, Brazil, and China, they do not grow well in colder climates.
led to research on using other plant protein sources in other parts of the world. There has

also been examination of plants that are more useful for their chemical content than for food or clothing uses, but so far there has been little published research on these plants for their utility as adhesives. This may change if the biofuels market becomes more profitable, because the interest would be more in the oils and carbohydrates and not in the proteins. The main outlet for excess proteins has been primarily as animal feed and not as industrial chemicals.

5.4.1 WHEAT GLUTEN

Although wheat straw has been examined and commercialized as a replacement for wood in making composites for home buildings and furnishings, the proteins in the seeds have been examined on a limited extent as the main adhesive. Wheat gluten certainly plays a major role in food products, given its cohesive and adhesive nature. Nonetheless, the protein content of wheat is low compared with that for other protein sources. Additionally, understanding wheat proteins is complex because of the many varieties of wheat. Besides the main divisions of hard grain (durum) wheat and soft grain wheat, there are many genetic variations, different growing conditions, and a variety of processing conditions [61]. The hard grain wheat gives strong doughs used in pizza making, whereas the soft grain wheat gives weak, extensible doughs used in cookie making Breads use grains in the middle range. With more than 100 different proteins in wheat, they are grouped into categories based on their

structure and properties [61]. Analysis of the proteins by size exclusion high-performance liquid chromatography shows a continuum of peaks from monomeric to polymeric, making separation of pure proteins difficult Among the monomeric (single-chain) proteins are the gliadin and albumin groups. The gliadins are monomeric storage proteins with molecular weights of 30-80 kpa. whereas the monomeric albumins have weights of 20-30 kpa, with many of them being enzymes (amino acid composition shown in Table 5.4). Compared with soy, wheat proteins are high in glutamate plus glutamic acid and proline, and low in aspartame plus aspartic acid and lysine among

TABLE 5.4
Amino Acid Content in Weight Percentage of the Main Wheat Proteins

Amino Acid	Glutenin	Gliadin	Albumin, Monomeric
Alanine	4.4	3.3	8.4
Arginine	3.0	2.0	5.7
Aspartate+aspartic acid	3.7	2.8	7.6
Cysteine	2.6	3.3	8.1
Glutarnate+glutarnic acid	28.9	34.6	10.8
Glycine	7.5	3.1	8.3
Histidine	1.9	1.9	0
Isoleucine	3.7	4.3	1.7
Leucine	6.5	6.9	7.6
Lysine	2.0	0.6	5.0
Methionine	1.4	1.2	2.6
Phenylalanine	3.6	4.3	0.1
Proline	11.9	16.2	7.5
Serine	6.9	6.1	6.4
Threonine	3.4	2.4	2.4
Tryptophan	1.3	0.4	3.0
Tyrosine	2.5	1.8	3.4
Valine	4.8	4.8	11.3

Source: MacRitche, F. and Latiandra,,D., Structure and functionality of wheat proteins, in: *Food Proteins and Their Applications,* S. Darnodaran and A. Paraf (Eds.), pp. 293-325, Marcel Dekker, New York, 1997.

the reactive amino acids. The other major group is the polymeric (aggregated) proteins containing three groups (glutenins, high molecular weight albumins, and triticins). The glutenins make up about 85% of the polymeric proteins, and are similar to the gliadins in amino acid composition, but glutenins are made up of many different types of aggregates with a wide range of molecular weights. The gliadins are high in proline and low in lysine, as is the glutenin. The high molecular weight albumins are mainly amylases, whereas the criticism are globular proteins. These proteins are unusually low in glutamate plus glutamic acid and low in aspartate plus aspartic acid compared with other plant proteins.

Although a lot of research has been done on separation of proteins using a variety of analytical techniques, the main evaluation of protein properties has been in dough mixing and property tests [61]. The ability of gluten to hold dough together indicates that these proteins may have some utility as an adhesive. Wheat Hour contains 75%-85% starch and only 10%-15% proteins (wheat gluten) [61]. Therefore, the Hour is of limited value as an adhesive unless there is a co reactant that decreases the water sensitivity of the starch. The natural occurrence is for the starch to be in granules and the protein more in the continuous phase. Although the protein is only a small part of the composition, being part of the continuous phase, it has a large impact on the physical properties of the dough.

Due to these limitations, there has been research on using wheat flour as an adhesive. By far the biggest use has been to provide tack in wood adhesives, such as PF, because wheat gluten imparts the stickiness in doughs. Therefore, it is not surprising that it provides tack to wood adhesives. Some adhesives, such as phenolics and isocyanate used in wood bonding, are often not tacky enough to hold the layers together in plywood, fibers in fiberboard, particles in particleboard, or strands in OSB prior to hot pressing and curing Gluten has been examined as an adhesive for particleboard [62], wood panels [631, and two-ply veneer bonds as an alternative to SPI under basic conditions [64]. Characterization of wheat glutens in relation to bond strength of two-ply veneer bonds was also carried out [65]. Prior work has not shown gluten to be a superior adhesive to soy in these applications.

5.4.2 Rapeseed and Canola

Although rapeseed readily grows in many areas, its use as an agricultural product has been limited of the toxic nature of the plant [66,67]. The amino acid content of rapeseed, given in Table 5.5, is not very different from the soy protein in most functionalized amino acids in comparison with the data in Table 5.2. Although the proteins are not influenced by the toxic components, these components have limited the processing of the plant for commercial applications. High erucic acid content limited the use of the oils, because erucic acid has been associated with cardiac lesions, and the carbohydrates contain glucosinolates responsible for metabolism disruption in cattle and pigs. The oil is still useful for lubrication and other purposes, and the plant is used for winter ground cover.

As with many oilseeds, rapeseed is dried, crushed, and derailed to produce rapeseed meal. The meal is treated to decrease toxicity and used as animal feed. Although the toxins limit the food use of rapeseed, these toxins do not hinder the use of the meal or Hour as an adhesive. Rapeseed proteins can be isolated from the meal, using a process similar to other oilseeds. Dispersing the meal in water at pH 11-12 dissolves the proteins, allowing them to be separated from insoluble meal components using centrifugation [67,70].For rapeseed, sodium sulfite is added to limit oxidation of the phenolic compounds, which may then react with the proteins [71]. The supernatant is first acidified to pH 3.5-4 with dilute acid to precipitate the protein and then separated from the soluble carbohydrates and other soluble compounds by centrifugation. Given the limited or nonexistent human consumption, rapeseed flour is not readily available in the United States, and instead, most workers have used the meal of rapeseed or canola because of its availability. Rapeseed has also been treated with formaldehyde as a plywood adhesive [72].

Research in Canada led to the production of canola in 1979, a cultivar of rapeseed with oil low in erucic acid and meal with a low content of glucosinolates [66,67]. Additional cultivars have also been developed. The ability to use all parts of canola has supported an increase in total rapeseed

TABLE 5.5
Amino Acid Content in Weight Percentage of Rapeseed Protein and Canola Protein

Amino Acid	Rapeseed Protein	Canals Protein
Alanine	5.2	4.4
Arginine	10.2	5.8
Aspartate+aspartic acid Cysteine	13.8	7.3
Glutamate+glutamic acid Glycine	1.5	2.4
Histidine	21.2	18.1
Isoleucine	6.0	4.9
Leucine	2.8	3.1
Lysine	4.8	4.3
Methionine	8.2	7.1
Phenylalanine	5.8	5.6
Proline	2.3	2.0
Serine	3.3	4.4
Threonine	5.9	3.8
Tryptophan	5.6	4.0
Tyrosine	5.3	4.4
Valine	NA[a]	1.3
	NA[a]	3.2
	6.2	5.5

Source: Josefsson, E., J. *Sci. Food Agric.*, 21, 99-103, 1970; Canola Council of Canada, http://www.canolacouncil.org/oil-and-meal/canola-meal/nutrient-composition-of-canola-meal/protein-and-amino-acids/.

[a]*NA:* not available..

production from 19.2 million tn. in 1985 to 72.5 million tn. in 2013. Rapeseed oil is used for biodiesel fuel and lubricants, as well as in food in the form of canola oil. Because canola is a variant of rapeseed, the proteins are similar to those in rapeseed and are mainly globular [67]. As shown in Table 5.5, the amino acid composition is similar between rapeseed and canola, but there is less aspartate plus aspartic acid and glutamate plus glutamic acid in canola. Acid- and base-hydrolyzed canola meal was examined as an additive for bonding fiberboard [73]. Canola protein isolate was used to bond cherrywood veneer at 190°C to give good wet bond strength in two-ply wood bonds. The addition of sodium bisulfite to decrease the dimercaptan bonds and viscosity did not greatly decrease bond strength [74]. Given the amounts of rapeseed and canola grown, and that these are a ready source of protein, it is surprising that more research has not been done on them.

5.4.3 LUPINE

Lupine is a legume that has been used for food for thousands of years. It is a common plant in North and South America, around the Mediterranean Sea, and in Australia [75]. In some places, it is often used for its decorative flowers, but it is also harvested in a number of countries as a food in various forms. Although it has not received the attention that the soybean has, it is used as flour in South American and European countries. The ability of lupine to grow in soils and climate unfavorable to soybeans has led to studies on improving its yield Selection and modern agriculture practice has increased its protein and oil content, and made it worth considering economically [76]. Lupine has been compared with soy because of the similar properties of high protein content and protein

TABLE 5.6
Amino Acid Content in Weight Percentage of Lupine Proteins

Amino Acid	Lupine Flour	Lupine Globulins	Lupinc Albumins
Ailaline	3.1	2.7	3.6
Alanine	11.1	11.8	12.6
Arginine Aspartate+	10.8	10.6	12.6
aspartic acid	2.2	1.5	1.7
Cysteine Glutamate	25.1	27.4	26.6
+glutamic acid	4.0	3.7	2.0
Glycine	2.1	1.8	2.1
Histidine Isoleucine	4.3	4.5	3.8
Leucine	7.3	7.4	7.6
Lysine Methionine	4.4	3.9	5.4
Phenylalanine Proline	0.5	0.3	0.5
Serine	3.9	3.9	3.2
Threonine Tryptophan	4.1	4.4	4.1
Tyrosine	5.2	5.4	5.3
Valine	3.9	3.1	5.0
	0.4	0.5	0.2
	4.6	5.6	1.8
	3.4	3.2	3.6

Source: Duranti, M. and Cerletti, P., *J. Agr. Food Chem.*, 27, 977-978, 1979

composition (Table 5.6), except that the glutamate plus glutamic acid content is higher than aspartate plus aspartic acid in lupine, whereas the opposite is true for soy (Table 5.3). The proteins in lupine are mainly globulins with some albumins [76].

Lupine seed or bean proteins are 87% globulins and 13% albumins [78]. Of the globulins, 44% are vicilin-like, 33% are legumin-like, and 23% are others [76]. The vicilin proteins are storage gobulins, have molecular weights between 143 and 335 kDa, and are all glycoproteins, whereas the legumin-like globulins are larger in size and do not have attached carbohydrates. The albumins have been less characterized

Limited work has been done on bonding wood with lupine adhesives, but two studies indicate that they are about equal to soy adhesives in bond strength withlower dispersion viscosities [79.80].

5.4.4 COTTONSEED

Cotton is grown and used for its fiber, but the seeds need to be removed first; Whitney's cotton gin, one of the most famous inventions, removes the seeds from the cotton, which eliminated hand separation. Since the seed is mainly a low-value but abundant by-product, research has been carried out to find a use for the cotton seed protein that is of higher value than being used in animal feeds. As with many other plant proteins, it has been investigated as an adhesive for wood bonding. Cottonseed meal proteins are fairly typical in composition for plant proteins, but have a higher arginine content (Table 5.7).

He and coworkers have looked at the performance of cottonseed protein isolate in plywood Bonding [82,83], whereas Cheng et al. looked at the performance of the meal for producing wood composites [84]. There are insufficient data available to compare the cottonseed proteins with the soy proteins as wood adhesives.

TABLE 5.7

Amino Acid Content in Weight Percentage of Cotton Seed Meal Proteins

Amino Acid	Cottonseed Meal	Amino Acid	Cottonseed Meal
Alanine	4.5	Lysine	4.4
Arginine	11.5	Methionine	1.8
Aspartate+aspartic acid	10.1	Phenylalanine	5.7
Cysteine	1.6	Proline	4.3
Glutamate + glutamic acid	21.7	Serine	4.7
Glycine	4.9	Threonine	3.6
Histidine	2.8	Tryptophan	NA[a]
Isoleucine	3.4	Tyrosine	3.4
Leucine	6.6	Valine	5.1

Source: O'Mara, F.P. et al., J. *Ant`tn. Sci.,* 75. 1941-1949. 1997.

[a]NA. not available.

5.5 MILK (CASEIN AND WHEY)

5.5.1 CASEIN

Milk is an important source of proteins with some industrial uses, but mainly food uses. Although early recorded history does not indicate much use of milk as an adhesive, it has been used as a binder in milk paint. This type of binder has been used for thousands of years and is still commercially available. Although milk itself is not used as an adhesive, because of the high fat and sugar content, the proteins from it have had good adhesive utility. Generally, the proteins are separated from milk into casein and whey protein fractions, with the casein being more commercially important, whether it is separated as the isolated casein or used for cheese and yogurt production. Casein and whey proteins have different amino acid compositions (Table 5.8), but the real differences are molecular weights, protein conformation, and phosphorylation of the casein protein. Native casein is a complex micelle that has two purposes in milk besides the nutritional value of the protein, which are binding and dispersing calcium phosphate and butterfat in milk [85]. These two functions are located in different portions of the casein micellar structure. Calcium binding appears to be associated with phosphorylated serine residues in localized domains [85]. The second function involves having the polar groups localized in the protein sequences so that the rest of the chain is quite hydrophobic to hold the butterfat in the milk. The large casein micelles give milk its opaqueness and provide stability to the milk at different temperatures and pH conditions. The casein is known to have low crystallinity (lack of α-helices and β-sheets) because of the high content of proline and hydroxyproline (not normally part of the protein analysis) (Table 5.8). These data counter the idea that crystallinity in soy is important for its adhesion. The main whey components are β-lactoglobulin, α-lactalbumin, and other low molecular weight proteins that provide low dispersion viscosities. The cow milk protein that has been used commercially as a wood adhesive is the casein-type adhesive from skim milk. The casein protein has been produced only in New Zealand for many years because of excess milk production and low cheese manufacturing there [88]. The dispersed casein micelle consists of casein proteins, calcium phosphate, and fat. The casein protein is isolated from milk by acid precipitation, using either inorganic acids (hydrochloric or sulfuric) or lactic acid produced from lactose by enzymatic reaction. The casein proteins are not just a source of amino acids for the growing calf, but also provide calcium that is bonded to the phosphorylated serine residues in the casein protein micelle. Sensitivity to acid is built into the casein micelles, allowing the

TABLE 5.8

Amino Acid Content in Weight Percentage of Cow's Milk, Case in Protein, and 80% Whey Protein Concentrate

Amino Acid	Milk	Casein	Milk Whey 80% Concentrate
Alanine	2.3	2.76	5.55
Arginine	3.8	3.35	2.71
Aspartate+aspartic acid	5.8	7.57	9.18
Cysteine	0.3	Part of methionine value	
Glutamate+glutamic acid	21.7	21.85	15.84
Glycine	0.4	1.73	5.32
Histidine	2.3	2.54	0.78
Isoleucine	6.0	4.59	4.97
Leucine	10.8	8.89	10.66
Lysine	6.9	7.75	8.81
Methionine	2.9	3.20	7.97
Phenylalanine	5.5	10.14	5.82
Proline	9.8	9.33	6.66
Serine	5.4	5.54	5.30
Threonine	4.4	4.05	6.87
Tryptophan	6.0	1.04	1.73
Tyrosine	1.2	Part of phenylalanine value	
Valine	6.6	5.64	1.84

Source: Macy. I.G. et al., The composition of milks. A compilation of the comparative composition and properties of human, cow, and goat milk, in: *Colostrum and Transitional Milk*, National Academy of Sciences and National RRarch Council, Washington. DC, 1953; Sindayikengera. S. and Xia, W.-S., *Jhejiang Univ. Sci. B*, 7 (2), 90-98,, 2006..

complex to break apart in stomach acid, freeing up the components. Although the isolation process irreversibility breaks up the protein micelle, it leaves protein aggregates that have both a large hydrophobic side and a polar side with phosphorylated groups. This aggregate is made up of four types of casein proteins, with three of them containing substantial amounts of serine phosphate, along with a negative charge at pH 6.6, and the fourth one being glycosylated [85].

The precipitated acidic casein is converted into an adhesive using a combination of sodium hydroxide and calcium oxide [1,891. The pH is raised from the isoelectric point of about 4.5 to greater than 12, usually using a mixture of sodium hydroxide and lime [85,891. The sodium provides greater solubility, but is poor in water resistance, with the opposite being true for the calcium. The slowly dissolving lime is added shortly before use to the sodium caseinate, to prevent viscosity from getting too high prior to application. Among the additives for casein adhesives were soy to lower cost and blood to give better wet strength [43,89901. Except for blood proteins, the caseinate adhesives produced the most water-resistant protein adhesive of the twentieth century. This adhesive was used for making exterior plywood and propellers for wooden airplanes, especially in World War I, often with blood mixed in. It was also used in early glulam beams, because of its strength and good water resistance. In fact, it was recently reported that casein-bonded glulam beams were used in an unheated and non-air-conditioned building for 75 years before the building was disassembled and the beams tested for strength [91]. Most of the designed strength was retained.

The price and limited availability of casein has held back any further development in this area. Casein adhesives continue to be used in certain applications such as the construction of fire-resistance doors.

5.5.2 WHEY

After precipitating the casein from milk, whey is processed to separate the proteins from the lactose, fats, and minerals. However, most of the whey comes not from casein precipitation from low-fat milk, but from cheese or yogurt production using high-fat or low-fat milk. The whey proteins have been divided into three classes, based on the conditions used to separate them from the casein portion. The first is from hard cheese production, which uses rennet coagulation of milk at pH 6.6. The second is from soft cheese production, which uses acid coagulation of casein, and cottage cheese production. A newer area is the acidic whey from yogurt production. Unless the protein is concentrated, these whey products have more lactose than protein, because most of the lactose goes into the whey. Conversely, the fat content of the whey fraction is not very high, because most of the fat goes into the cheese or yogurt portion.

Whey concentrate has most of the nonprotein materials removed, and the isolate is even purer (its amino acid composition is given in Table 5.8). The concentrates are generally made by ultrafiltration of the whey (<25% protein) to allow the low molecular weight organics, especially lactose and fat, and inorganics, to be removed [92]. However, the range of products is quite varied in protein content (3O%-8O%), depending on the degree of filtration. Further purification leads to a whey protein isolate that is 90%-95% protein. In addition to ultrafiltration, ion exchange has been used to purify the whey proteins.

Although whey contains many proteins with diverse functions, all of the proteins are globular, with the |3-lactoglobulin and the a-lactalbumin accounting for about 70% of the protein weight l93]. The b-lactoglobulin has a molecular mass of 18.3 kpa with 43%-5O% of proteins in b-sheets. 10%-15% in a-helices, and l5%-20% in b-turns. It is a compact dimer molecule with two disulfide bridges. The a-lactalbumin has a low content of organized sheets of 30% a-helix and 9% b-sheets. with one bound calcium ion and four disulfide bridges. These proteins also contribute to most of the hydration, gelling, and surface-active properties of the whey proteins. The immunoglobulins ar a heterogeneous family of glycoproteins from 148 to 1000 kpa and tend to be heat sensitive. The other main protein is bovine serum albumin with 582 amino acids. Other minor proteins can play an important role in the properties of whey [93].

Whey products are used in a wide variety of food products, including animal feed [93]. Whey has also been tested as a wood adhesive with an aqueous polymer isocyanate for glulam [94].

5.6 EGG WHITE

All parts of the egg contain proteins with concentrations of 3% of the shell, 11% of the white, an 17.5% of the yolk. For a long time, egg whites were used as binders for paints, but there was n record of them being used as an adhesive. Although eggs are mainly used as a food source, the whites can also be a source for nonfood, industrial applications. The whites do not completely drain out of the eggshells in industrial egg processing, and the remaining egg whites washed from the eggshells cannot be used for food applications because of health concerns. This leaves these whites available for industrial uses.

Ovalbumin is a high percentage of the protein in egg whites, and is also easy to separate from the other egg components in a very pure form [95,961. The ovalbumin is a monomeri phosphoglycoprotein with four cysteine and one cystine amino acid in 385 amino acids [95,97] The different ovalbumins vary in the amount of phosphorylation at the two specific serine sites. The more stable ovalbumin forms have a 92.50C denaturation temperature, compar with 84.50C for a less stable form. Although most analytical methods do not show a difference, the more stable ovalbumin is slightly more compact. The four cysteine residues in the native protein are not very accessible, preventing them from joining together as disulfide. This could change after denaturation. Table 5.9 shows that the ovalbumin, egg white, and egg yolk do not have large differences in amino acids, except that the glutamate plus glutamic acid am

cysteine are greater in the ovalbumin than in the egg white and greater in the egg white than in the egg yolk.

Gelation in water is important to food properties, and shows the development of structure caused by heat. In some ways, it is similar to the structure that provides water resistance to protein adhesives after hot bonding of the adhesives. Gel properties of the ovalbumin have been extensively studied and shown to be sensitive to the gelation conditions [95]. Heat gelation is apparently driven mainly by hydrophobic interactions between protein molecules, rather than by hydrogen bond or disulfied formation. At higher pH conditions, in which the electrostatic repulsion is greater, the gel is similar to a closely packed string of beads with each protein molecule being a bead. At low concentrations, sol structures form, whereas at higher concentrations, cross-links develop to form a three-dimensional network, with both types of structures being transparent. As the pH is decreased near the piezoelectric point or as the ionic strength of the aqueous phase increases, the gel structure becomes random aggregates and is less linear, with these gels being opaque. The opaque gels have greater strength than the transparent gels.

Despite the extensive studies in the last century on egg proteins for food uses and some uses of egg as a binder, the wood adhesive properties of egg proteins had not been reported until recently [99]. Compared with most other proteins, dispersions of ovalbumin are low in viscosity. This could be caused by the monomeric nature of ovalbumin rather than polymeric protein aggregates of most of the proteins. Although their viscosities are low, ovalbumin dispersions provide good wet and dry bond strengths without any coreactant [99]. The aqueous dispersions of dried egg white are almost as good as those of the ovalbumin, but those of the dried egg yolk are much poorer and those of the dried whole egg are in between the whites and yellow portions of eggs. These differences in adhesive strength are not obvious if one solely depends on making predictions from the amino acid contents in Table 5.9.

TABLE 5.9
Amino Acid Content in Weight Percentage of Ovalbumin, Egg White, and Egg Yolk

Amino Acid	Ovalbumin	Egg White	Egg Yolk
Alanine	5.7	5.9	5.1
Arginine	5.9	5.7	7.0
Aspartate + aspartic acid	9.2	7.7	8.5
CysteinCysteine	8.0	2.4	1.7
Glutamate + lutamate + glutamic acid	15.7	13.8	12.2
Glycine	3.2	3.6	3.6
Histidine	2.4	2.1	2.3
Isoleucine	7.1	6.3	6.2
Leucine	9.9	8.6	8.5
Lysine	6.4	5.9	6.7
Methionine	5.4	3.8	2.6
Phenylalanine	7.5	6.3	4.5
Proline	3.8	3.7	4.5
Serine	8.5	6.8	8.2
Threonine	5.7	4.4	5.2
Tryptophan	NA[a]	1.5	1.5
Tyrosine	3.8	4.1	4.7
Valine	6.1	7.6	7.0

Source: C et al., *J. Biol. Chem* , 186, 23-35, 1950.

[a]NA not available

5.7 COLLAGEN

5.7.1 ANIMAL (BONES AND HIDES)

Animal glues are the earliest recorded adhesives used in wood bonding. Ancient Egyptian drawings demonstrated veneer bonding with a hot-melt adhesive such as collagen [1]. Seed, milk, or egg proteins provide essential nutrients to young organisms for growth, but collagen-based animal proteins are used for structural purposes during the entire life span of the animal. Instead of individual protein chains being coiled globules, the collagen protein forms elongated triple-stranded helical coils [1001. These coiled proteins that make up the collagen fibrils provide not only good strength but also good flexibility. The high contents of proline and hydroxyproline prevent the protein chain from forming a globular shape, and the many polar groups provide good interaction between the chains. Therefore, coils are helically linked together [25,100]. The different protein contents for animal and fish collagen are given in Table 5.10.

It is important to understand how different these protein adhesives are from most of the other proteins discussed in this chapter. The amino acid composition in Table 5.10 is highly nonpola; 125,103]. Thus, it would appear that the protein should be globular in nature to minimize water interaction, yet the high contents of proline and hydroxyproline not only prevent the protein from folding into a globular structure, but instead generate a helical structure. Some globular proteins can be converted into a more fibrous structure under certain processing conditions [104], but do not exist that way in nature. Although globular proteins are generally dispersible without modification, fibrous collagens need to be broken apart by chain separation with some polymerization cc be dispersed in water. The degree of chain separation and polymerization generally has a larger effect than the source on the performance of these adhesives, leading to the different grades main determined by viscosity and gel hardness values [100]. These extended proteins behave similarly

TABLE 5.10
Amino Acid Content in Weight Percentage for Animal and Fish Collagen

Amino Acid	Animal Hide Collagen	Fish Collagen
Alanine	11.0	10.4
Argln'ine	8.8	9.1
Aspartate + aspartic acid	6.7	7.5
Cysteine	0	0
Glutamate + glutamic acid	11.4	11.4
Glycine	27.5	28.2
Histidine	0.8	9.1
Hydroxyproline	14.1	8.3
Isoleucine	1.7	1.6
Leucine	3.3	3.2
Lysine	4.5	3.7
Methionine	0.9	2.3
Phenylalanine	2.2	2.0
Proline	16.4	12.4
Serine	4.2	7.9
Threonine	2.2	3.3
Tryptophan	NA[a]	NA[a]
Tyrosine	0.3	0.6
Valine	2.6	2.3

Source: Eastoe, J. E., *Biochem. J.*, 61, 589-600, 1955; Eastoe, J. E., *Biochem. J.*, 65, 363-368, 1957
[a]NA: not available

to a typical synthetic polymer with greater interchain interactions and greater influence by a wide variety of additives [25,100,103]. These interchain interactions are not only polar in some domains but should also be hydrophobic in other domains, given the high concentrations of the nonpolar glycine, proline, alanine, and other nonpolar amino acids [25]. The protein chains are still in a helical shape, and these helices tend to reform intertwined structures [I0O]. The extended structure allows for a greater ability to formulate products with a wider variety of performance characteristics than is possible with the globular proteins. Thus, it is important to consider the effect of the primary structure, or polypeptide backbone, on the properties of the protein (globular or extended) and the ability to modify the protein properties for the adhesives.

There is tremendous variability in the collagen, depending on its source (skins, connective tissue, cartilage, or bones) and the age and type of animal source (type and raising of cattle, type of pigs). The main source has been the hides and bones of beef cattle [103]. The bones and hides are processed using different procedures, because of the need to separate the collagen from other different materials. After cleaning to remove most of the inorganic and other organic molecules, the fibrils are disentangled and hydrolyzed using an inorganic acid and heat [103]. The source of the collagen and the hydrolysis conditions determine the properties of the adhesive, although the difference in source becomes less critical as the chains are shortened to lower the molecular weight of coiled proteins [100]. These proteins are mainly sold on the basis of viscosity, color and gel strength measurement. The average molecular weight of these hydrolyzed proteins is in the range of 29-250 kDa. Increasing the molecular weight generally increases the viscosity and adhesive strength [l00], with the higher molecular weights yielding gels that need to be heated for application.

The original animal glues were sold in the dry state and then dispersed in hot water to provide a thick solution. In the solution state, the adhesive is not stable for extended periods of time. Therefore, the adhesive is made up just prior to using it. This is basically a hot-melt adhesive, because it needs to be heated for application, and then the initial strength is obtained as the adhesive cools. The initial strength is provided by a high propensity of these coiled polymers to associate, forming a gelled network that provides high initial strength by cooling for holding the substrates together. The strength rapidly increases as some of the water is lost to evaporation or absorption into the substrate. Further strength is provided as the gel forms a more entangled network and additional water moves away from the bond line [100,103]. Strong bonds form in the dry state, because of the intertwined protein chains and extensive hydrogen and hydrophobic bonds between the coiled proteins. There can also be polar bond formation between the acidic and basic groups, with a reported tensile strength of up to 69 MPa (10,000 lb./in.2) [25]. The dried film forms a continuous, noncrystallizing film that resists most solvents and oils.

To avoid the necessity of dissolving the dry glue in hot water, liquid animal glues have been developed using gel-depressant chemicals. These chemicals limit the association of the proteins in water, allowing the gelled state to be postponed [100,1O3]. As the water departs from the glue, the gel-depressant nature of these additives disappears and a strong bond is formed. The addition of glycerin plasticizers results in jelly adhesives that provide products with permanent flexibility [103]. For nonwarping applications such as bookbinding, the jelly glues are mixed with plasticizers, extenders, and fillers to provide a fast-setting product with limited shrinkage after drying.

The affinity of animal glues for water leads to poor water resistance, which can be either a disadvantage or an advantage. Certainly, the adhesives' tendency to soften and, in some cases, to delaminate is usually a disadvantage. However, this is useful when a recyclable adhesive is desired; the adhesive is strong in the dry state but softens for adhesion with water treatment and dissolves away with more extensive water exposure. Moisture sensitivity can be decreased by precipitating the protein with inorganic sulfates, borates, or formaldehyde [103]. These adhesives were used with paper products, gummed tapes, and coated abrasives, as well as with wood for furniture construction and woodworking industries. These adhesives were initially displaced by polyvinyl acetate) adhesives or white glues. Now, there are a variety of synthetic polymers, such as cross-linking poly(vinyl acetate) and polyurethane, types that are easier to use and provide greater bond durability. The

main use of animal adhesives today is in historic preservation and by hobbyists who want to use traditional methods [IOO].

5.7.2 FISH

Fish glues are, in many ways, similar to animal glues. but are often in a separate category because of property and performance differences. Fish glues are liquid at room temperature. This provides an advantage compared with animal glues, which originally were solids that needed to be dissolved in hot water and applied hot to prevent gelation prior to application [1051. Although more recent versions of animal glue are made in liquid form, there is still a difference between animal and fish glues [l00]. Liquid fish glue can bond a wide variety of substrates (metal, rubber, glass, cement, cork, wood, and paper) and will not soften up to 2600C. However, they do soften in water, which allows them to be used in self-sticking stamps and as a temporary adhesive.

The adhesive comes from the skins and bones of fish, especially cod skins, by extraction with hot water, and is concentrated to about 45% solids [l05]. Cleanliness of the processing near the fish processing plant and use of added deodorant helps keep the product low odor. The glues are between 30 and 60 kpa in molecular weight, although some gelatin versions are higher in molecular weight [I0O]. The fish glues can be more linear than animal glues, leading to greater water solubility. After drying, the glues have internal stresses because of volume shrinkage; this shrinkage can increase with higher humidity conditions, which leads to both greater interchain helix formation and increased brittleness. Fish amino acid contents from bones and skin are similar to that of animal collagens in having unusually high amounts of proline and hydroxyproline (Table 5.l0).

Because the protein is atmospheric, it has a certain buffering capability, but pH levels below 3 and above 9 should be avoided because of degradation of the protein. Fish glue has shown sirengths of 32 MPa (4641.2 sibling) with 50% wet wood failure in ASTM D905 wood shear testing (ASTM International, West Conshohocken, PA). Their liquid nature and high strength led to their use in furniture. However, the brittle aspect of the glue can lead to failure with time. Fish glue's water solubility can be decreased by adding polyvalent salts, such as aluminum or ferric sulfates, oxidation with chromate s, or adding aldehyde cross-linkers, such as formaldehyde, glyoxal, or glutaraldehyde ll05]. Because of their compatibility with many waterborne polymer dispersions, fish glue has been added to these dispersions to increase their tackiness. As with other collagen adhesives, fish glues are still used today by hobbyists and furniture restorers.

5.8 BLOOD

Not surprisingly, blood is one of the wood adhesives that goes back to the beginning of recorded history, because of its ability to dry into a strong material with adequate water resistance. Blood became a common adhesive for wood bonding in the twentieth century because it provided good exterior durability. Fresh blood was used for a long time, because blood does not keep well under ordinary conditions. The use of blood expanded greatly between 1910 and 1925 with the development of a low-temperature method of drying the blood without decreasing its solubility and the need for water-resistant plywood for military aircraft [I]. Most blood adhesives require heat curing, limiting their use in plywood, which was often cold-cured These adhesives were generally displaced by phenolics in the 1930s, but the need for more water-resistant interior plywood led to a revival of blood adhesives as wet-strength enhancers. Because of their high cost and variability, blood proteins were often used with other proteins. The use of blood in wood adhesives peaked at 22.7 Gg (50 million lb.) in the 1960s and steadily declined to near zero. Although the data on amino acid content in Table 5.11 are for guinea pig blood, the data for other blood sources are not very different. The lysine content is high while the combined aspartate and glutamate are low compared with soy protein.

TABLE 5.11

Amino Acid Content in Weight Percentage of Blood Proteins from Guinea Pig

Amino Acid	Blood	Hemoglobin	Plasma
Alanine	7.6	9.0	6.5
Arginine	4.5	2.6	6.1
Aspartate + aspartic acid	10.2	10.0	10.3
Cysteine	2.1	NA[a]	3.8
Glutamate + glutamic acid	12.5	7.1	16.9
Glycine	3.8	4.1	3.5
Histidine	6.5	9.1	4.4
Isoleucine	3.4	3.2	3.6
Leucine	6.8	12.5	2.3
Lysine	9.9	9.5	10.2
Methionine	1.4	0.9	1.8
Phenylalanine	7.3	5.0	6.7
Proline	5.0	3.0	6.5
Serine	5.5	5.7	5.4
Threonine	3.7	6.8	1.2
Tryptophan	NA[a]	NA[a]	NA[a]
Tyrosine	3.2	0.8	5.0
Valine	6.8	7.7	6.1

Source: Chang, Y.-Y.H, and Judson, C.L., Compr. Biochem. Physiol., 62A, 753-755, 1979.
[a]NA: not available.

There are three general categories of dried blood [1O7]. The most important as an adhesive is soluable blood, which is the most dispersible protein for good water-resistant bond strength after heat curing. The heat is minimized in the drying of the blood by using a spray or vacuum dryer. For inclusion in this category, more than 80% of the protein needs to be soluble. The other extreme is insoluable heat-dried blood that has low solubility (less than 20%) and leads to gritty dispersions; this is the most common form today and used by gardeners. The remaining category of partially soluble blood is between these extremes. Blood was mainly used to enhance the water-resistance properties of other protein adhesives. The casein-blood adhesives were considered the most durable for exterior plywood [90,107] until PF adhesives were eventually formulated to provide a better adhesive. Blood was also used with soy adhesives to improve their properties. For many years, blood was added to PF adhesives to improve their properties, including foamability and tack. Although blood improved the moisture resistance of protein adhesives, it had to be dried to prevent degradation. Not only was there a large difference between pig and cattle blood, but the blood varied with the breed and time of the year. This difference mainly showed up in the rheology of the adhesive, which needed formulation adjustments with new blood batches.

Although blood has not been used much for adhesives, there could be some availability in the future as by-products when blood is used as the source of specific chemicals [108]. Although this would not be a large volume, blood was generally added in small amounts to other proteins and synthetic adhesives to improve tack and, in some cases, water resistance.

5.9 SYNTHETIC AND MODIFIED PROTEINS

One study has shown that specific sequences of synthetic polypeptides can provide better adhesives than other sequences [109]. Given the difficulty of making these proteins, this type of process does

not currently have commercial viability. However, testing hypotheses of protein interactions with synthetic proteins could be very interesting scientifically.

Although protein glues have always been derived from natural sources, this does not mean that they cannot be improved, for example, by genetic manipulation Genetic modification is a significant area now for many crops to improve resistance to various insects, diseases, and pesticides used to treat the crop. Other genetic modifications have provided the canola variant of rapeseed and high oleic content soybeans. Although these changes have not been directed toward changing the pro- teins, changing other properties of the crop can lead to inadvertent changes in the proteins, some of which may be beneficial.

Biomimicry and bioinspired are two newer approaches for product development The difference between them is that biomimicry attempts to carry out a function in the same manner as is done in nature, whereas bioinspired approaches use principles learned from natural systems but with different chemistry or structure. An interesting biomimetic approach is to incorporate 3,4-dihydroxy-L-phenylalanine CL-DOPA) amino acid into the protein, so that when exposed to oxygen, the dihydroxybenzene group forms the hydroquinone. Two of these hydroquinones on different chains can then couple to cross-link the polyamide chains. The L-DOPA can also form bridges by chelating metals. For a biomimetic approach, Liu and Li successfully grafted dopamine to a commercial soy protein isolate (CSPI) via an amide linkage imparting DOPA-like phenolic functional groups found in marine adhesive protein. a strong and water-resistant adhesive [1101. For a bioinspired approach. they also successfully grafted cysteine onto CSPI by amide linkages. increasing the content of the -SH group significantly [III]. The free mercapto group content in soy protein could greatly increase the strength and water resistance of wood composites bonded with the modified soy protein. Mussel protein contains a high amount of mercapto-containing cysteine.

5.10 PROSPECTS

Some protein sources that were used as wood adhesives in the past are not likely to be available in suitable volume and with viable cost. Many of these proteins have found other uses in human or animal food or specialty chemicals. Although the technology developed in the early twentieth century. for protein adhesives was suitable at the time for making bonded wood products, this technology is not capable of meeting today's production or performance criteria for wood products. This emphasizes the need for novel technology for using proteins. Professor Li at Oregon State University has developed the most new routes steadily so proteins [48.54,55,57,80,I 10,11I]. Additional creativity
more protein adhesives that can better compete with synthetic adhesives.

Although protein adhesives provide good dry strength, many are deficient in wet strength. Today much more is known about protein structure and more ways are known for modifying proteins Unfortunately, chemical modifications are often not well coordinated with what is known about protein structure. The work with soy (e.g., the much higher strength for the commercial isolate compared with the native isolate) and egg whites (e.g., the much lower viscosity of egg protein at high solids compared with soy) shows that there is untapped potential in proteins that may hopefully be converted into stronger adhesives by properly controlling the colloidal and coalescence properties The polyamidoamine-epichlorohydrin co reactant demonstrates that a good co reactant can make soy proteins commercially viable adhesives. Hopefully. with a better understanding of the proteins. structures and the colloidal properties, the desired properties can be achieved.

5.11 SUMMARY

Proteins serve many purposes in nature, such as adhesives, enzymes, structural tissue, and amino acid sources for growing organisms. Both plants and animals have been sources of protein for wood adhesives. Although proteins had dominated the wood bonding market for centuries

starting in the 1940s fossil fuels became the dominant source of adhesives for wood bonding because of their durability, ease of use, and relatively low cost. This trend may be reversing for a variety of reasons, with concern about formaldehyde emissions from UF being chief among them. The concern about hydrocarbon cost and the desire for higher biobased-content products are additional drivers.

Although some of the most effective protein adhesives, such as casein and blood adhesives, are no longer available at reasonable prices and volumes, some other protein sources have good availity and prices. Principal among these more abundant proteins are plant-based proteins that have an infrastructure in place to grow, gather, and process the crop. In many cases, protein is the lower-value portion of the crop, with the oil of oilseeds being more valuable than the meal or flower.

However, native proteins by themselves have not shown sufficient strength in most cases when the bonded samples are exposed to wet conditions. Proteins will need to be physically or chemically modified or used with a coreactant to provide sufficient cohesive strength to be able to withstand wet conditions. The improved products can be developed empirically, as in the past, or systematically by understanding the colloidal nature of proteins. Taking leads from food chemistry and adopting the knowledge developed by bioscientists, who study natural protein products, will be critical to allow the work to be done more systematically.

A lot of development was needed to make phenolic, amino, and isocyanate types of adhesives suitable for wood bonding. The original polyvinyl acetate) adhesives had good adhesion but poor moisture resistance. The cross-linked versions were developed later to provide the adhesives with much improved water and heat resistance. Hence, the protein adhesives need to be considered as starting materials, not finished products. The success with Soyad adhesives from Solenis and the Purebond wood products made by Columbia Forest Products are signs that the right chemistry can help soy adhesives overcome their deficiencies.

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REFERENCES

1. A. L. Lambuth. Protein adhesives for wood, in Handbook of Adhesive Technology. 2nd edn. A. Pizzi and K. L. Mittal (Eds.), pp.
2. C. R. Frihart and M. J. Birkeland. Soy properties and soy wood adhesives, ACS Symp. Seri. 1178, 167-192(2014).
3. G. E Myers. Effects of temperature and humidity on formaldehyde emission from UF-bonded boards: A literature critique. Forest Prod. J. 35 (9). 20
4. C. R. Frihart, J. M. Wescott, T. L. Chaffee and K M. Conner. Formaldehyde emissions from urea-formaldehyde- and no-added-formaldehyde- bonded particleboard as influenced by temperature and relative humidity. Forest Prod. J. 62 (7-8), 551-558 (2012).
5. A. Pizzi. Urea-formaldehyde adhesives. In: Handbook of Adhesive Technology, 2nd edn, A. Pizzi and K. L. Mittal (Eds.).
6. G. E. Myers. Formaldehyde emission from particleboard and plywood paneling: Measurement, mechanism and product standards. Forest
7. G.E Myers and M. Nagaoka, Emission of formaldehyde by particleboard: Effect of ventilation rate and loading on air-contamination levels. Forest Prod J 31 (7), 39-44 (1981).
8. G. E. Myers. How mole ratio of UF resin affects formaldehyde emission and other properties: A literature critique. Forest Prod. J. 34 (5), 35-41 (1984).
9. S. Zhang, J. Li, J. Zhang, Y. Li and Q. Gao. Study on properties of modified low molar ratio urea-formaldehyde resins (I). Adv. Mater. Res 113-114, 2016-2020 (2010).
10. EP. Formaldehyde. February 26. http:/Iwww.epa.gov/formaldehyde. Accessed March 4, 2016 (2016).

11. ARB. Composite Wood Products ATCM 2016. Formaldehyde emissions in wood products. http://www.arb.ca.gov/toxics/compwood/compwood.htm. Accessed March 4, 2016 (2016).
12. Chimar-Hellas. Update on Formaldehyde Emissions from Wood-based Panels. http;//www.chimarhellas.com/wp-content/uploads/2008/07/formaldehyde_2008.pdf. Accessed February 12, 2016 (2008).
13. Intertek. ATCM: Reducing Formaldehyde Emissions from Composite Wood Products. https://www.google.com.br/?gfe_rd=cr&ei=Y2bbVtn2lcHK8geo85SgCA&gws_rd=ssl#q=formaldehyde+emissions+wood+products. Published June 22, 2010. Accessed December 20, 2015.
14. M. J. Birkeland, L. Lorenz, J. M. Wescott and C. R. Frihart. Determination of native (wood derived) formaldehyde by the desiccator method in particleboards generated during panel production. Ho/dorschung 64 (4), 429-433 (2010).
15. J. B. Wilson. Life-cycle inventory of particleboard in terms of resources, emissions, energy and carbon Wood Fiber Sci. 42 (CORRIM Special Issue), 90-106 (2010).
16. HSE. P43 Using Isocyanate-based Adhesives. COSHH Essentials for Printers 05/07. http://www.hse.gov.uk/pubns/guidance/p43.pdf. Accessed March 22, 2016 (2007).
17. E. W. Lusas. Oilseeds and oil-bearing materials. In: Handbook of Cereal Science and Technology, K Kulp and G. Points, Jr. (Eds.), pp. 297-362, Marcel Dekker, New York (2000).
18. D, K Salunkhe. J. K Chavan and R. N. Adsule. World oilseed Chemistry, Technology, and Utilization Van Nostrand Reinhold, New York (1991).
19. W. J. Wolf. Soybeans and other oilseeds. In: Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edn, Vol. 21, pp. 417-442, Wiley, New York (1983).
20. R. Lasztity. Chemistry of Cereal Proteins, CRC Press, Boca Raton, FL (1995).
21. S. Damodaran. Food proteins: An overview. In: Food Proteins and Their Applications, S. Damodaran and A. Paraf (Eds.), pp. I-24, Marcel Dekker, New York (1997).
22. T. E. Creighton. Proteins: Structure and Molecular Principles, W.H. Freeman and Company, New Yod (1984).
23. J. I. Boye, C.-Y. Ma and V. R Harwalkar. Thermal saturation and coagulation of proteins. In: Fox Proteins and Their Applications, S. Damodaran and A. Paraf (Eds.), pp. 25-56, Marcel Dekker, New York (1997).
24. S. Damodaran and A. Paraf (Eds.). Food Proteins and Their Applications, Marcel Dekker, New York (1997).
25. C. L. Pearson. Animal glues and adhesives. In: Handbook of Adhesive Technology, 2nd edn, A. Fizz and K L. Mittal (Eds.). pp. 283-298, Marcel Dekker, New York (1994).
26. Y. V. Wu and G. E. Inglett. Denaturation of plant proteins related to functionality and food applications a review. J. Food Sci. 39, 218-225 (1974).
27. Y. Wang, M. Sarkar, A. E. Smith, A. S. Krois and G. J. Pielak. Macromolecular crowding and protein stability. J. Am. Chem Soc. 134, 16614-16618 (2012).
28. P. K Nandi. Chemical and physical methods for the characterization of proteins. In: Food Protein and Their Applications, S. Damodaran and A. Paraf (Eds.), pp. 597-602. Marcel Dekker, New Yon (1997).
29. K. Nishinari, Y. Fangs, S. Guo, and Q G. Phillips. Soy proteins: A review on composition, aggregation and emulsification Food Hydrocolloids 39, 301-318 (2014).
30. V. B. Tolstoguzov. Protein-polysaccharide interactions. In: Food Proteins and Their Applications. S Damodaran and A. Paraf (Eds.). pp. 171-198, Marcel Dekker, New York (1997).
31. D. Oakenfull, J. Pearce and R. W. Burley. Protein gelation. In: Food Proteins and Their App/ication." S. Damodaran and A. Paraf (Eds.), pp. 111-142, Marcel Dekker, New York (1997).
32. W. R. Egbert. Isolated soy protein: Technology, properties, and applications. In: Soybeans as Functio Foods and Ingredients, K Liu (Ed.), pp. 134-162, AOCS Press, Champaign, IL (2004).
33. I. F. Laucks. Little journeys into the chemurgies industries: Soybean adhesives. The Chemurgic Digest (20) 173-176 and (21) 185-188 (1943).
34. A. L. Lambuth. Soybean glues. In: Handbook of Adhesives, 3rd edn, I. $heist (Ed.), pp. 172-180, V Nostrand Reinhold, New York (1990).
35. X. S. Sun. Isolation and processing of plant materials. In: Bio-Based Polymers and Composites, R Wool and X. S. Sun (Eds.), pp. 33-55, Elsevier-Academic Press, Burlington, MA (2005).
36. E. M. Bainy, S. M. Tosh, M. Corredig, V. Poysa and L. Woodrow. Varietal differences of carbohydrates in derailed soybean Hour and soy protein isolate by-products. Carbohydrate Po/ym. 72, 66 (2008).
37. X. S. Sun. Thermal and mechanical properties of soy proteins. In: Bio-Based Po/ynzers and Contras` R. P. Wool and X. S. Sun (Eds.), pp. 292-326, Elsevier-Academic Press, Burlington, MA (2005).

38. S. Utsumi, Y. Matsumura and T. Mort. Structure-function relationships of soy proteins. In: *Food Proteins and Their Applications*, S. Damodaran and A. Paraf (Eds.), pp. 257-291. Marcel Dekker. New York (1997).
39. D. Fukushima. Recent progress of soybean protein foods: Chemistry, technology. and nutrition. Fo*od Rev. Int*. 7 (3), 323-351 (1991).
40. J. E. Kinsella, S. Damodaran and B. German. Physiochemical and functional properties of oilseed proteins with emphasis on soy proteins. In: *New Protein Foods: Seed Storage Proteins*, A. M. Altschul and H. L. Wilcke (Eds.), pp. 108-179, Academic Press, New York (1985)
41. X. S. Sun. Soy protein polymers and adhesion properties. *J. Biobased Mater. Bioenergy* 5. 1-24 (2011)
42. Agriculture and Consumer Protection. Soybean Protein Concentrate, http:www.fao.orrg/docrep/to523e/ tO532e06.htm. Accessed October 1, 2015 (2006).
43. C. Bye. Casein and mixed protein adhesives. In: *Handbook of Adhesives*, 3rd edn. I. Skeist (Ed.), pp. 135-152, Van Nostrand Reinhold, New York (1990).
44. P. H. Steele, R. E. Kreibich, P. J. Steynberg and R. W. Hemingway. Finger jointing green southern yellow pine with a soy-based adhesive. *Adhes. Age* 41 (10),49-56 (1998).
45. M. Sterley. Adhesive systems for green gluing, finger jointing of green Scots pine. In: *Green Gluing of Wood Process - Products - Market*, COST E-34, BorAs.,Sweden, B. K8llander (Ed.), SP Swedish National Testing and Research Testing Institute, Stockholm, Sweden (2005).
46. M. Lipke. Green glued hngerjoint wall studs: Industrial experience of Hampton Lumber Mills, Inc. In: *Green Gluing of Wood - Process - Products - Market*. COST E-34, BorAs, Sweden, B. Kallander (Ed.), SP S SP Swedish National Testing and Research Testing Institute. Stockholm, Sweden (2005).
47. N. S. Hettiarachchy, U. Kalapathy and D. J. Myers. Alkali-modified soy protein with improved adhesive hydrophobic properties. *J. Am. Oil Chem. Soc.* 72, 1461-1464 (1995).
48. J. Huang and K Li. A new soy Hour-based adhesive for making interior type 11 plywood. *J. Am. Oil Chem.. Soc.* 85, 63-70 (2008).
49. N. Ji .J. Long, H. Y. Zheng and J. Q. He. Phenolic resin modified soybean protein adhesive. *Adv. Mater. Res*. 236-238, 3-7 (2011).
50. U. Kalapathy, N. S. Hettiarachchy, D. Myers and K. C. Rhee. Alkali-modified soy proteins: Effect of salts and disulfide bond cleavage on adhesion and viscosity. *J. Am. Oil Chem. Soc*. 73, 1063-1066 (1966)
51, U. Kalapathy, N. S. Hettiarachchy and K C. Rhee. Effect of drying methods on molecular properties m functionalities of disulfide bond-cleaved soy proteins. *J. Am. Oil Chem. Soc.* 74, 195-199 ((1997).
52. M. Kuo. D. Adams, D. Myers, D. Curry, H. Heemstra, J. L. Smith and Y. Bian. Properties of wood/ a agricultural fiberboard bonded with soybean-based adhesives. *Forest Prod. J.* 48 (2), 71-75 (1998).
53. J. Wescott and C. R. Frihart. Water-resistant vegetable protein adhesive dispersion compositions. U.S. Patent 7345136, assigned to Heartland Resource Technologies LLC and U.S. Department of Agriculture (2008).
54. K. Li, S. Peshkova and X. Geng. Investigation of soy protein-kymene® adhesive systems for wood composites. *J. Am. Oil Chem. Soc*. 81, 487-491 (2004).
55. K. Li. Formaldehyde-free nitrocellulose adhesives and composites made with the adhesives. U.S. Patent 7252735. assigned to Oregon State University (2007).
56. C. R. Frihart, M. J. Birkeland, A. J. Allen and J. M. Wescott. Soy adhesion that can form durable bonds for plywood, laminated wood flooring and particleboard. In: *Proceedings of the International Conventionn of Society of Wood Science and Technology and United Nations Economic Commission for Europe -Timber Committee*, Geneva, Switzerland, WS-20 (2010).
57. Y. Jang and K. Li. An all-natural adhesive for bonding wood. *J. Am. Oil Chem. Soc.* 92, 431-438 (2015)
58. M. J. Birkeland, R. Wu and S. S. Weaver. Adhesive materials and methods of forming lignocellulosic composites using such adhesive materials. U.S. Patent Appl. 20150151449 Al, assigned to Design Adhesives Inc. (2014).
59. X. S. Sun. Soy protein adhesives In: *Bio-Based polymers and Composite*s, R. P. Wood and X. S. Sun (Eds.), pp. 327-368, Elsevier-Academic Press, Burlington, MA (2005).
60. D.Vnuĉec , A. Kutnar and A. Goršek. Soy-based adhesives for wood-bonding: A review. *J. Adhes. Sci. Technol.* 31, (8) 910-931 (2017). http://dx.doi.org/10.1080/01694243.2016.1237278. Accessed September 26, 2016.
61. F. MacRitche and D. Lafiandra. Structure and functionality of wheat proteins. In: *Food Proteins and Their Applications*, S. Damodaran and A. Paraf (Eds.), pp. 293-325, Marcel Dekker, New York (1997).
62. S. Khosravi, F. Khabbaz, P. Nordqvist and M. Johansson. Protein-based adhesives for particleboards *Ind. Crop. Prod.* 32, 275-283 (2010).

63. H. Lei, A. Pizzi, P. Navarrete. A. Redl and A. Wagner. Gluten protein adhesives for wood panels. In: Wood Adhesives, A. Pizzi and K. L. Mittal (Eds.), pp. 353-366, CRC Press, Boca Raton. FL (2010).
64. P. Nordqvist, F. Khabbaz and E. Malmstr0m. Comparing bond strength and water resistance of alkali-modified soy protein isolate and wheat gluten adhesives. Int. J. Adhesion Adhesives 30, 72-79 (2010).
65. P. Nordqvist, P. E. Johansson, F. Khabbaz and E. Malmstr6m. Characterization of hydrolyzed or heat treated wheat gluten by SE-HPLC and 13C NMR: Correlation with wood bonding performance. *Ind. Crop. Prod*. 51. 51-61 (2013).
66. Wikipedia. Rapeseed (2016). httpsJ12 /en.wikipedia.org/wiki/Rapeseed. Accessed March 2, 2016
67. S. H. Tan, R. J. Mailer, C. L. Blanchard and S. O. Agboola. Canola proteins for human consumption: Extraction, profile, and functional properties. *J. Food Sci*. 76, R16-R27 (2011).
68. E. Josefsson. Glucosinolate content and amino acid composition of rapeseed (*brasszca napus*) meal as affected by sulphur and nitrogen nutrition. *J. sci. Food Agric*. 21, 99-103 (1970).
69. Canola Council of Canada. Protein and Amino acids. (2016). http://www.canolacouncil.org/oil-and-meal/canola-meal/nutrient-composition-of-canola-meal/protein-and-amino-acids/. Accessed June 1, 2016.
70. G. Mieth, J. Bruckner, J. Kroll and J. Pohl. Rapeseed: Constituents and protein products part 2: Preparation and properties of protein-enriched products. *Nahrung* 27 (8), 759-801 (1983).
71. Y. M. Tzeng, L. L. Diosady and L. J. Rubin. Production of canola protein materials by alkaline extraction, precipitation, and membrane processing *J. Food Sci*. 55, 1147-1151 (1990).
72. D. Narayanamurti, V. Ranganathan and D. C. Roy. Rapeseed protein-formaldehyde dispersions as ply-wood adhesives. Indian Forest Leaflet No. 58, Forest Research Institute, Debra Dun, India (1943).
73. I. Yang, G.-S. Han, S. H. Ahn, I.-G. Choi, Y.-H. Kim and S. C. Oh. Adhesive properties of medium-density fiberboards fabricated with rapeseed Hour-based adhesive resins. *J. Adhes*. 90, 279-295 (2014).
74. N. Li, G. Qi, X. S. Sun, M. J. Stamm and D. Wang. Physicochemical properties and adhesion mance of Canola protein modified with sodium bisulfite. *J. AM. Oil Chem. Soc.* 89, 897-908 (2012).
75. Wikipedia, Lupinus. (2015). httpsJ' /en.wikipedia.org/wiki/Lupinus. Accessed March 2, 2016.
76. M. Duranti. The structure of lupine seed proteins. Nahrung 30 (3-4),221-227 (1986).
77. M. Duranti and P. Cerletti. Amino acid composition of seed proteins of *lupinus albus*. *J. Agr. Chem.* 27, 977-978 (1979).
78. P. Cerletti. Lapin seed proteins. In: *Developments in Food Proteins*, B. J. Hudson (Ed.), pp. 133-171, Applied Science Publishers, London (1983).
79. M. Vidal, E. Vergara, M. N08ez, A. Ballerini and E. Ramirez. Evaluation of lapin Hour (LF)-based adhesive for making sustainable wood materials. In:*Proceedings of the International Convention of Society of Wood Science and Technology and United Nations Economic Commission for Europe - Timber Committee*. Geneva, Switzerland Society of Wood Science and Technology, Monona. WI(2010).
80. K. Li and J. Huang. Development and characterization of a formaldehyde-free adhesive from lupine flour, glycerol, and a novel curing agent for particleboard (PB) production. *Holzforschung*, 70 (10). 927-935 (2016).
81. F. P. O'Mara, J. J. Murphy and M. Kath. The amino acid composition of protein feedstuffs before and after ruminal incubation and after subsequent passage through the intestines of dairy cows. *J. Anim. Sci.* 75, 1941-1949 (1997).
82. Z. He, D. C. Chapital and H. N. Cheng. Comparison of the adhesive performances of soy meal,water washed meal fractions, and protein isolates. *Modern Appl. Sci.* 10 (5), 112-120 (2016).
83. Z. He, D. C. Chapital, H. N. Cheng and M. K Dowd. Comparison of adhesive properties of water- and phosphate buffer-washed cottonseed meals with cottonseed protein isolate on maple and poplar veneers. *Int. J. Adhes. Adhes*. 50, 102-106 (2014).
84. H. N. Cheng, M. K. Dowd and Z. He. Investigation of modified cottonseed protein adhesives for wood composites. *Ind. Crop. Prod* 46, 399-403 (2013).
85. D. G. Dalgleish. Structure-function relationships of caseins. In: *Food Proteins and Their Applications*, S. Damodaran and A. Paraf (Eds.), pp. 199-224, Marcel Dekker, New York (1997).
86. I. G. Macy, H. J. Kelly and R. E. Sloan. The composition of milks. A compilation of the comparative composition and properties of human, cow, and goat milk. In: *Colostrum and Transitional Milk*, National Academy of Sciences and National Research Council, Washington, DC(1953).
87. S. Sindayikengera and W.-S. Xia. Nutritional evaluation of caseins and whey proteins and their hydrolysates from Protamex. Jhejiang Univ. sci. B 7 (2), 90-98 (2006).
88. C. R Southward. Casein products. *111-Dairy-E-Casein*, 13 (1998). http://nzic.org.nz/ChemProcesses/dairy/3E.pdf. Accessed June 15, 2016.
89. H. K Salzberg. Casein glues and adhesives. In: *Handbook of Adhesives,* 3rd edn, I. Skeist (Ed.). pp. 158-171. Van Nostrand Reinhold New York (1990).

90. W. D. Detlefsen. Blood and casein adhesives for bonding wood In: Adhesives from Renewable Resources, R. W. Hemingway, A. H. Conner and S. J. Branham (Eds.). pp. 447-452, American Chemical Society, Washington, DC(1989).
91. D. R. Rammer. J. de Melo Moura and R. J. Ross. Structural performance of the second oldest glued-laminated structure in the United States. In: Proceedings of the Structures Congress 2014, Boston, MA, pp. 1233-1243 (2014).
92 H. M. Jayaprakasha and Y. C. Yoon. Production of functional whey protein concentrate by monitoring the process of ultrafiltration. Asian-Australasian. J. Anim. Sci. 18, 433-438 (2005).
93. P. Cayot and D. Lorient. Structure-function of whey proteins. In: Food Proteins and Their Applications, S. Damodaran and A. Paraf (Eds.). pp. 225-256, Marcel Dekker, New York (1997).
94. Z. Gao. W. Wang, Z. Zhao and M. Guo. Novel whey protein-based aqueous polymer-isocyanate adhesive for glulam. J. App/. Po/ym. Sci. 120, 220-225 (2011).
95. E. Doi and N. Kitabatake. Structure and function of egg proteins. In: Food Proteins and Their Applications, S. Damodaran and A. Paraf (Eds.). pp. 325-340, Marcel Dekker, New York (1997).
96. A. C. Awade, s. Moreaua, D. Mollk, G. Brulkb and J.-L. Maubois. Two-step chromatographic procedure for the purification of hen egg white ovomucin, lysozyme, ovotransferrin and ovalbumin and characterization of purified proteins. J. Chromatogr. A 677, 279-288 (1994).
97. M. Zemser, M. Friedman, J. Katzhendler. and L. L. Greene. Relationship between functional properties and structure of ovalbumin. J. Protein Chem. 13, 261-274 (1994)
98. J, C. Lewis, N. S. Snell., D. J. Hirschmann and H. Fraenkel-Conra. Amino acid composition of egg proteins. J. Biol. Chem. 186, 23-35 (1950).
99. C. R. Frihart, H. Satori, Z. Rongxian and M. J. Birkeland. Ovalbumin as a wood adhesive. In: Proceedings of the 37th Annual Meeting of The Adhesion Society, San Diego, CA (2014).
100. N. C. Schnellmann,. Animal glues: A review of their key properties relevant to conservation. Rev. Conserv. 8, 55-66 (2007).
101. J E. Eastoe. The amino acid composition of mammalian collagen and gelatin. Biochem. J. 61. 589-600 (1955).
102. J. E. Eastoe. The amino acid composition of fish collagen and gelatin Biochem. J. 65, 363-368 (1957).
103. J. R. Hubbard. Animal glues. In: Handbook of Adhesives, 3rd edn, I. $heist (Ed.), pp. 139-151.,Van Nostrand Reinhold, New York (1990).
104. H.-C. Huang The Production of Textile Fibers from Soy Proteins. iowa State University, Ames, IA. Retrospective Theses and Dissertations, Paper 10480. http://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=11479&context=rtd. Accessed December 20, 2016 (1994).
105. R E, Norland. Fish glues. In: Handbook of Adhesives, 3rd edn, I. Skeist (Ed.), pp. 152-157, Van Nostrand Renhold, New York (1990).
106. Y.-Y, H. Chang and C. L. Judson. Amino acid composition of human and guinea pig blood proteins, and ovarian proteins of the yellow fever mosquito aedes aegypti; and their effects on the mosquito egg production. Covnpr. Biochem. Physiol. 62A,753-755 (1979).
107. A. L Lambuth. Blood glues. In: Handbook of Adhesives, 3rd edn, I. Skeist (Ed.), pp. 181-191, Van Nostrand Reinhold, New York (1990).
108. C. S. F. Bah, A. E. D. A. Bekhit, A. Came and M. A. McConnell. Slaughterhouse blood: An emerging source of bioactive compounds. Con:pr. Rev. Food Sci. Food Saf. 12, 314-331 (2013).
109. X. Mo. Y. Hiromasa, M. Warner, A. N. Al-Rawi, T. Iwamoto. T. S. Rahman, X. Sun, and J. M. Tomich. Design of 11-residue peptides with unusual biophysical properties; Induced secondary structure in the absence of water. Biophys. J. 94, 1807-1817 (2008).
110. Y. Liu and K. Li. Chemical modification of soy protein for wood adhesives. Macromol. Rapid Commun. 23. 739-742 (2002).
111. Y. Liu and K. Li. Modification of soy protein for wood adhesives using mussel protein as a model: The influence of a mercapto group. Macromol. Rapid Commun. 25, 1835-1838 (2004).

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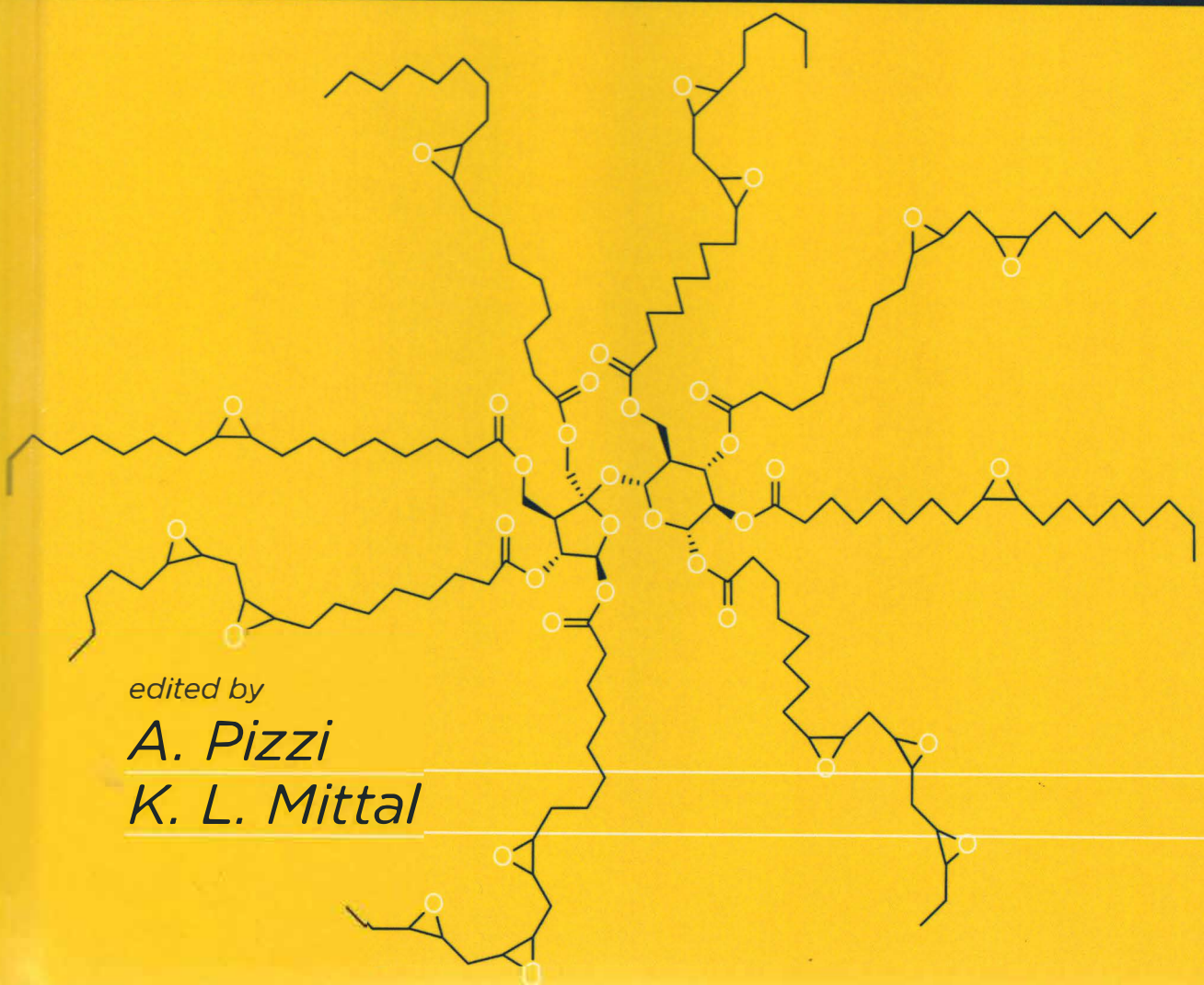

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