

Isoelectric pH of Polyamide–Epichlorohydrin Modified Soy Protein Improved Water Resistance and Adhesion Properties

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ABSTRACT: Protein macromolecules derived from plants have been considered as alternative resources for various applications, including adhesives, films, rubbers, and biocomposites. Plant protein polymers are pH sensitive and need to be modified to meet application performance. This study demonstrated interactions between polyamide–epichlorohydrin (PAE) and soy protein as affected by pH and temperature. PAE and soy protein molecules formed reversible ionic complexes at room temperature at a pH range of 4–9. The complexation interactions acted as physical crosslinking, which stabilized the soy protein structure and increased its denatu-

ration temperature and enthalpy. The viscosity of adhesives derived from the interaction of PAE and soy protein was affected significantly by the complexation formation, denaturation, and pH. The complexation interactions improved the adhesion properties of the PAE/modified soy protein. pH also played an important role in the adhesion performance, which was attributed to the pH dependence of the protein conformation and PAE/soy protein complexation interactions.
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Key words: adhesion; adhesives; proteins; rheology

INTRODUCTION

The demand for adhesives in the United States reached 15.2 billion pounds in 2004.¹ Most adhesives, such as hot-melt, emulsion, vinyl-based, rubber-based, acrylic, phenolic, amino, epoxy, and silicone adhesives, are from petroleum resources. Concerns have been raised in recent years about diminishing petroleum resources, environmental pollution, and health problems caused by the manufacture, transportation, storage, and use of these petroleum-based adhesives.^{1–8} Therefore, the development of environmentally friendly adhesives from renewable resources is becoming increasingly important. Soy protein has great potential to serve as an alternative to petroleum-based adhesives because of its structural uniqueness, abundance, renewability, and biodegradability.

Soy protein is a large macromolecule with a molecular weight ranging from 300 to 600 kD, depending on its structure and confirmation. Soy protein has

been considered an alternative material for various applications, including adhesives, films, rubbers, and composites.^{2–4} Monomers of soy protein contain the same amino acid residues as many other proteins and are linked by amide bonds into polypeptide chains. The polypeptide chains are associated and folded into a three-dimensional complicated structure by disulfide and hydrogen bonds. Most soy proteins are globulins containing about 25% acidic amino acids, 20% basic amino acids, and 20% hydrophobic amino acids. Soy protein has an isoelectric pH at approximately 4.5. The solubility of soy protein is lowest at its isoelectric point (pI).

Soy-protein-based adhesives were first developed in the early 1920s and were mainly formulated for plywood applications. However, soy protein adhesives were not used widely because of their relatively poor bond strength and water resistance. Efforts have been made in recent years to improve their adhesion strength and water resistance.^{4,9–19} In this study, polyamide–epichlorohydrin (PAE) was used as a modifier. PAE is a well-known, wet-strength resin widely used in the paper and pulp industry. It is prepared by the reaction of water-soluble polyamide with epichlorohydrin to form a water-soluble, cationic polymer with reactive azetidinium groups. The azetidinium group can react with active hydrogen groups, such as carboxyl, hydroxyl, and amino functional groups.^{20–23} These reactions can increase water resistance by the

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formation of an insoluble network coating around the surface and by the formation of crosslinkages between the resin and the substrate.²³ Li et al.¹⁹ prepared adhesives with 40% PAE, a cationic polymer as a crosslinking agent, and 60% soy protein polymers. The adhesion strength and water resistance of the PAE/soy protein adhesive were significantly improved compared to both PAE and soy protein alone. The authors attributed the improved properties to chemical reactions between PAE and soy protein at elevated temperatures.¹⁹

In this study, interactions between soy protein and PAE were investigated in a wide range of pH and temperatures. The effects of such interactions on adhesive performance were evaluated. The surface structure and charges of both PAE and soy protein polymer are sensitive to pH; interactions and reactions between PAE and soy protein should be significantly affected by pH. Complexation interactions and chemical crosslinking reactions between PAE and soy protein were studied with a spectrophotometer, conductivity meter, and differential scanning calorimeter to provide information for the better understanding of the mechanism of PAE modification of soy proteins as affected by pH.

EXPERIMENTAL

Materials

Soybean protein isolate (SPI), containing 88.3% (dry basis) protein and 5% moisture, was extracted from defatted soybean flour with 95% particles through a 100-mesh U.S. sieve ($\sim 150 \mu\text{m}$) with a protein dispersion index of 90 (100/90, Cargill, Cedar Rapids, IA) according to the pI precipitation method. PAE was provided by Hercules, Inc. (Wilmington, DE) as Kymene 557H aqueous solution. It had 12.5 wt % PAE, a density of 1.03 g/cm^3 , and a pH of 4.6–4.9. Tris hydroxymethylaminomethane (Tris) was purchased from Fisher Scientific (Pittsburgh, PA). Cherry wood veneer with dimensions of 50 mm (width) \times 127 mm (length) \times 3 mm (thickness) was purchased from Veneer One (Oceanside, NY).

Sample preparation

SPI powder (12 g) was suspended in 100 mL of distilled water at room temperature and stirred until a homogeneous solution was obtained. Then, the desired amount of PAE solution was calculated from the SPI dry-weight percentage and was added drop by drop into the agitating SPI solution at room temperature. White precipitates were formed. The pH of the adhesive slurry was then adjusted with 2N HCl or 2N NaOH solution.

The PAE/modified SPI slurry was brushed onto one end of a piece of cherry veneer (127 mm \times 50 mm) until

the entire area was completely wetted (ca. $2.5 \pm 0.3 \text{ mg/cm}^2$ protein solid concentration). To minimize the variation of solid content of adhesive on each piece of wood sample, a consistent brushing procedure was used. The area of application on each end was 127 mm \times 20 mm. Two pieces of such adhesive-brushed cherry veneer were allowed to rest at room temperature for 10 min and were then assembled and pressed at 170°C and 1.4 MPa for 5 min with a hot press (model 3890 Auto M, Carver, Inc., Wabash, IN).

Thermal properties

The thermal properties of the PAE/modified SPI adhesives were tested on a PerkinElmer Pyris-1 differential scanning calorimeter (PerkinElmer, Norwalk, CT). The instrument was calibrated with indium and zinc standards before the measurements, and all measurements were conducted under a nitrogen atmosphere. The adhesive slurry, prepared as described in the Sample Preparation section, was sealed in a large-volume, stainless-steel differential scanning calorimetry (DSC) pan with an O-ring, which prevented any water evaporation during the DSC scan. The weight loss of the adhesive sample after scanning was less than 0.15%. All samples were held at 20°C for 1 min and were then scanned to 150°C at 10°C/min. After that, the samples were quenched to 20°C, held for 1 min, and scanned again to 150°C at 10°C/min. The denaturation temperature (T_d) and denaturation enthalpy (ΔH_d) were obtained from the first scan.

To study the chemical reaction at elevated temperatures, the 15%-PAE-modified SPI adhesive slurry was heated to 240°C at 10°C/min, quenched to 20°C, and then heated again to 240°C. For comparison purposes, the same DSC method used for the slurry was also used for the dried 15%-PAE-modified SPI adhesive, which was dried at 50°C overnight with about 6.7% moisture content. To ensure that the hot-press pressure influenced the chemical reaction between the SPI and PAE, the oven-dried 15%-PAE-modified SPI adhesive was further treated at 170°C and 1.4 MPa with the hot press for 5 min, and then, the treated adhesive was used for DSC measurement.

Rheological properties

The rheological properties of the PAE-modified SPI adhesives were determined with a Brookfield programmable rheometer (DV-III+) equipped with a small sample adapter (SC4-21/13R, Brookfield Engineering Laboratories, Inc., Middleboro, MA). The PAE-modified SPI adhesive, prepared as described in the Sample Preparation section, was transferred into the sample holder of the rheometer, and its viscosity was recorded at a shear rate of 93.0 s^{-1} and at 25°C.

Shear strength

The cherry plywood assemblies were preconditioned at 23°C and 50% relative humidity (RH) for 48 h and were then cut into five specimens that were 20 mm wide. These five specimens were further conditioned for 5 days in a chamber at 23°C and 50% RH.

Lap shear tests of the cherry plywood specimens were carried out according to ASTM D 2339.²⁴ An Instron universal testing machine (model 4465, Canton, MA) with a crosshead speed of 1.6 mm/min was used. The shear strength at maximum load was recorded; each value presented is the mean of five specimens and was recorded as dry-adhesive shear strength. Failure mode and percentage of cohesive failure within the wood of the test specimen were also determined by observation with a magnifying glass.

Water resistance

Water-resistance testing was performed according to ASTM D 1183 and ASTM D 1151.^{25,26} Ten of the 20 mm wide specimens for each set of conditions were soaked in tap water at 23°C for 48 h. Then, five of specimens were taken out and dried at 23°C and 50% RH for 5 days. The shear strength of the soaked–dried samples was tested according to the same testing methods used for the dry-adhesive shear strength, as described previously. The remaining five specimens were tested immediately after they were removed from the water according the same testing procedures used for the dry-adhesive shear strength test, and these measurements were recorded as wet shear strength.

Boiling test

A boiling test was carried out according to ASTM D 5572.²⁷ Five of the 20 mm wide specimens for each set of conditions were soaked in boiling water for 4 h and then dried at 63°C for 20 h. The specimens were then boiled again for 4 h and cooled in running water at room temperature for 1 h. The specimens were tested immediately after they were removed from the cooling water, and these measurements were recorded as boiling wet shear strength.

Turbidity

SPI (0.1 wt %) Tris solution was prepared by the dissolution of SPI powder in 10 mM Tris solution. The desired amount of PAE aqueous solution was added drop by drop. White precipitate was formed. Then, 2N NaOH solution was added to adjust the pH to between 10 and 11 or until the slurry became clear. After that, the slurry was adjusted to various pH values with HCl solution, and its absorbance at 600 nm was

measured with a Hitachi U-2010 spectrophotometer (Tokyo). For the SPI sample modified with 15 wt % PAE, a 0.05 wt % SPI solution was used instead of a 0.1 wt % solution.

Conductivity titration

Conductivity titration was carried out on an Accumet AR20 pH/mV/conductivity meter (Fisher Scientific) equipped with a two-cell conductivity probe at 27°C. The concentration of the SPI solution was 1.0 wt %. The PAE solution had a concentration of 12.5 wt % and was gradually added to the SPI solution. Before titration, the PAE solution was adjusted to the same pH as the SPI solution (pH = 7.34). The same titration was also performed for distilled water without SPI as a control experiment.

RESULTS AND DISCUSSION

Complexation interaction

SPI has a typical pI of 4.5, at which point the negatively charged group is balanced with the positively charged groups, and the SPI has a net charge of zero on the surface of the protein body. SPI precipitates at pI. SPI bears a net positive charge at a pH lower than its pI, the positively charged SPI molecules repel each other, and the SPI dissolves in water. In a similar manner, SPI bears a net negative charge and dissolves in water at a pH above its pI. The SPI solution had a pH of about 7.2, and it was clear. However, precipitation was observed immediately after the addition of PAE (pH = 7.1 at 5% PAE). Interestingly, the precipitates dissolved after the pH was adjusted to above 9 or below 4 and then reformed after the pH was adjusted back to 4–9. To study this phenomenon, the turbidity of the PAE/SPI slurry was measured at various pH values.

The SPI had a maximum absorbance at approximately pH 4.5 (Fig. 1), which corresponded to its pI. This result was consistent with the published results.²⁸ With addition of PAE, two peaks appeared: one peak was located at about pH 4.5, and the other peak's location varied with PAE concentration from pH 5.4 for 3 wt % PAE to pH 6.1 for 10 wt % PAE (Fig. 1). Also, the peaks broadened, and precipitate appeared with the addition of PAE. For the SPI with 15 wt % PAE modification, the peak was so broad that it was hard to accurately determine its location (Fig. 1). Only part of the SPI molecules was bound, with the PAE forming the complex at lower PAE concentrations. The remaining SPI still exhibited the same properties as the native SPI, which corresponded to the peak at pH 4.3. The PAE-bounded SPI (the complex) exhibited a different pH dependence, which corresponded to the second peak.

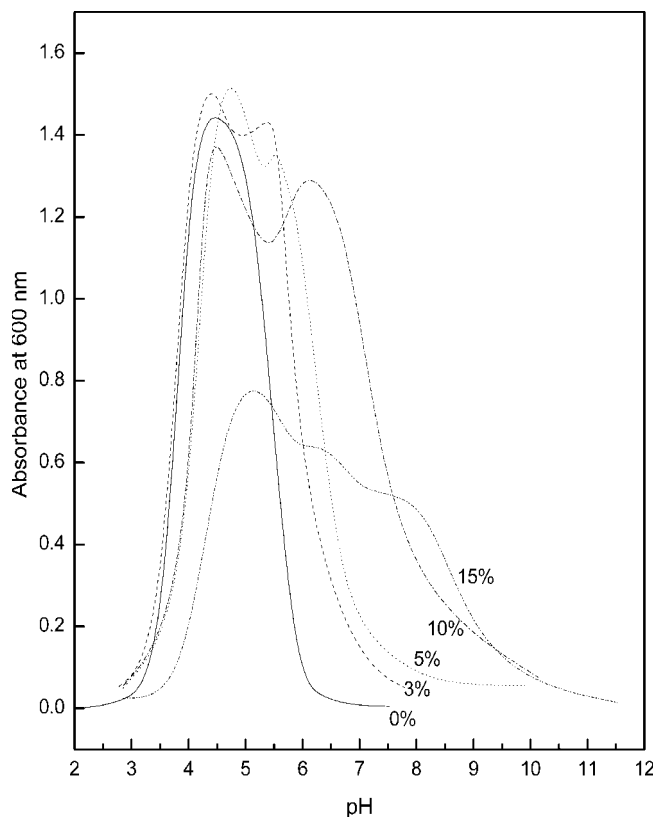


Figure 1 Absorbance profiles of the PAE-modified SPI in 10 mM Tris. The PAE concentrations in weight percentages are shown.

To further confirm the complexation formation due to the interaction between SPI and PAE, conductivity titration at pH 7.3 was carried out, as shown in Figure 2. The titration curve for the distilled water was a linear line, whereas the curve for the SPI solution showed a distinct transition point at a PAE volume of 700 μL , which corresponded to a PAE/SPI ratio of 22.5/100 by dry weight. It was hard to convert the weight ratio to a molar ratio because the SPI was a mixture of several protein fractions with different molecular weights. However, the slope change of the titration curve at 700 μL PAE was obviously due to the complexation between the SPI and PAE. SPI alone would not precipitate at the titration pH of 7.3. The data presented also indicate that there should have been no excess PAE in the adhesive system in the PAE range tested in this study.

PAE is a cationic polymer. After PAE was added to the SPI solution (pH \sim 7), the cationic part of PAE interacted with the anionic carboxyl group of the SPI to form PAE/SPI complexes [Fig. 3(B)]. SPI has a net negative charge at a pH of approximately 7.0. Although the PAE solution had a pH between 4.6 and 4.9, the incorporation of a small amount of PAE into the SPI solution would not significantly change the pH. It has been reported that PAE can react with

active hydrogen groups to form covalent bonds.^{20–23} In our opinion, however, such reactions would not happen at room temperature and/or under our experimental conditions (short time frame) because the turbid PAE/SPI slurry became clear when its pH was adjusted to basic (pH > 9) or extremely acidic (pH < 4) conditions. The driving force for the PAE/SPI complex was ionic interaction, and the complex formation was reversible on pH change. When the pH was adjusted to 9 or above, the abundant anionic OH^- groups in the adhesive slurry were bound to cationic groups of the PAE to release the PAE from the PAE/SPI complex and, hence, dissolved both components [Fig. 3(C)]. When the pH was adjusted to below 4, the carboxyl groups (COO^-) of SPI were bound to a proton ion (H^+) to form COOH groups and release SPI from the PAE/SPI complex and, hence, dissolved both components [Fig. 3(D)].

Thermal properties

Typical DSC thermographs of the 5%-PAE-modified SPI adhesives are shown in Figure 4, and the results are summarized in Table I. The DSC thermographs gave two endothermic transitions in the pH range 4.3–7.1, which were caused by the denaturation of the 11S and 7S components of the SPI, respectively.

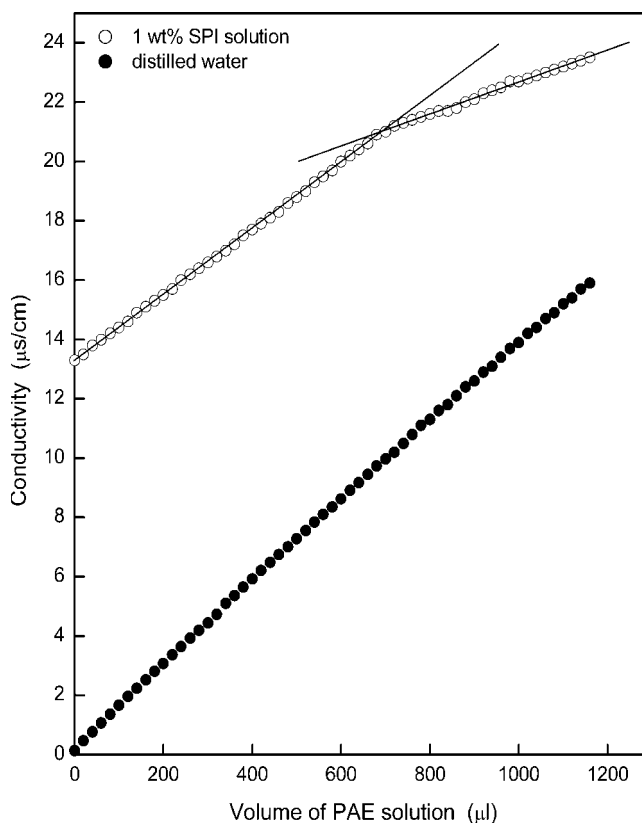


Figure 2 Conductivity titration curves of the 1 wt % SPI solution and distilled water with the PAE solution.

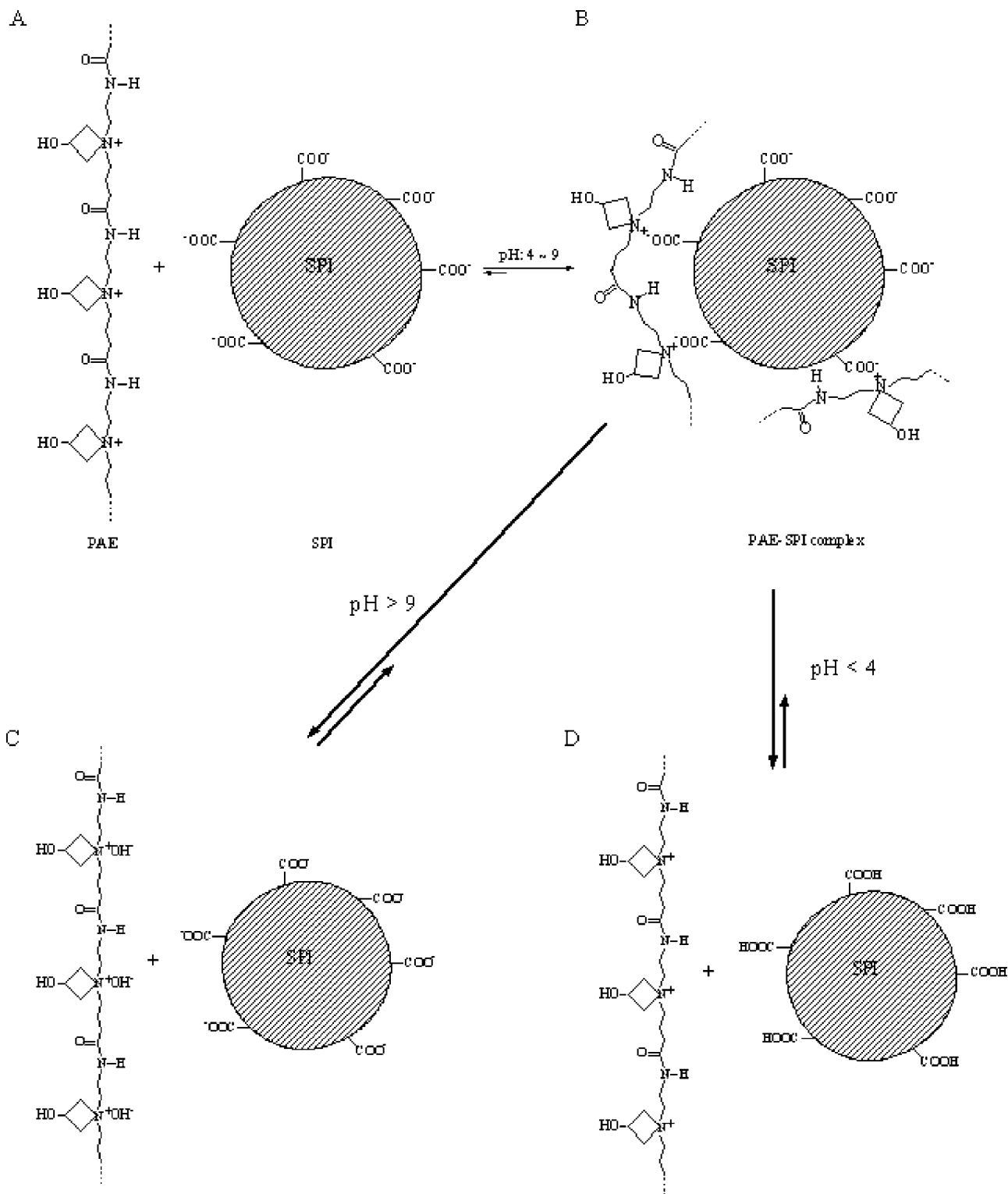


Figure 3 Schematic diagram of the formation of the PAE/SPI interpolymer complex and its disassociation.

T_d and ΔH_d varied with pH value. At the extremely basic condition (pH = 10.0) or extremely acidic condition (pH = 3.5), however, only one broad denaturation peak was observed (Fig. 4). ΔH_d also reached its highest value of 9.27 J/g at pH 7.1 (Table I),

which indicated that SPI was partly denatured at both extremely basic and acidic conditions.

The thermal properties of the SPI modified with various PAE concentrations are summarized in Table II. As PAE content increased, both T_d and ΔH_d

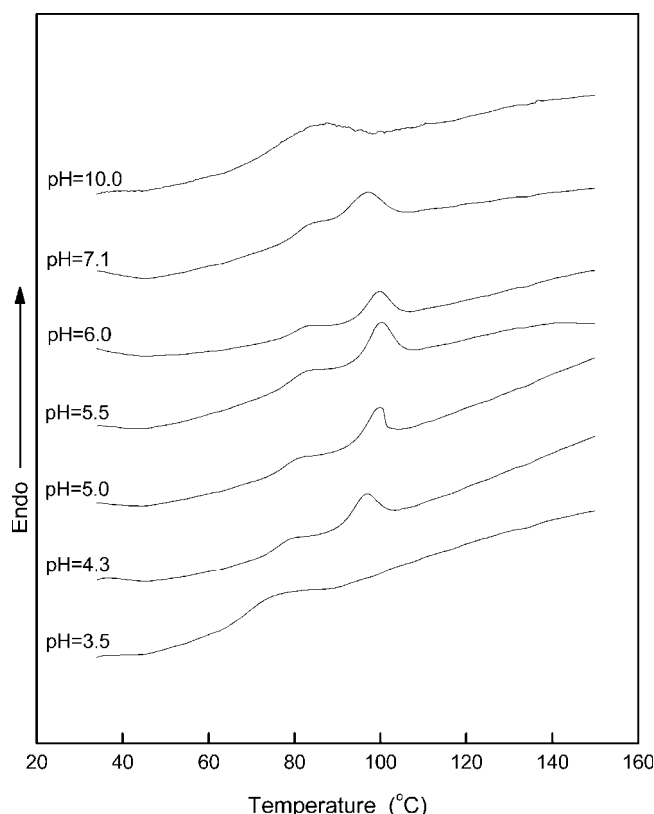


Figure 4 DSC thermographs of the 5 wt % PAE-modified SPI adhesives.

increased, which indicated that the structure of the soy protein was stabilized by the formation of the PAE/SPI complex. Soy protein has a typical globular structure, with most hydrophobic residues embedded and most hydrophilic residues exposed outside. Therefore, the cationic groups of PAE were bound to the exposed anion carboxyl groups of the SPI to form some kind of coating. Also, the ionic complexation interaction between PAE and SPI might provide an additional stable force for the soy protein structure and, hence, improve its heat resistance.

TABLE I
Thermal and Rheological Properties of the SPI Solution Modified by 5 wt % PAE at Various pH Values

pH	T_d (°C)		ΔH_d (J/g of SPI)	Viscosity (mPa s)
	T_{d1}	T_{d2}		
3.5	73.1	—	5.04	19.0
4.3	77.3	94.9	6.66	5.7
5.0	79.1	97.7	7.25	7.3
5.5	81.1	98.3	8.91	7.3
6.0	81.4	97.9	8.06	18.7
7.1	81.7	94.8	9.27	33.0
10.0	82.3	—	8.43	18.0

SPI/water = 12 : 100. The amount of PAE was based on SPI weight. Viscosity was measured at 25°C and at a shear rate of 93.0 s⁻¹.

TABLE II
Thermal and Rheological Properties of the SPI Solution Modified by Various Concentrations of PAE at pH 7.1

PAE concentration (wt %)	T_d (°C)		ΔH_d (J/g of SPI)	Viscosity (mPa s)
	T_{d1}	T_{d2}		
0	75.6	91.8	9.01	11.3
3	81.0	93.3	9.23	11.3
5	81.7	94.8	9.27	33.0
10	82.6	95.7	10.07	12.0
15	82.6	95.5	11.05	7.7

SPI/water = 12 : 100. The amount of PAE was based on SPI weight. Viscosity was measured at 25°C and at a shear rate of 93.0 s⁻¹.

Rheological properties

The apparent viscosity of the 5% PAE-modified SPI adhesives reached a minimum value at pH values ranging from 5.5 to 4.3 (Table I). The viscosity increased in both pH directions, either above 5.5 or below 4.3. However, the viscosity decreased again after pH 7.1 and up to pH 10.0 (Table I). Many factors affected the viscosity of the PAE/SPI adhesives, including as isoelectric precipitation, denaturation, and complexation formation. As previously discussed, the 5% PAE-modified SPI adhesives had a maximum precipitation at pH values ranging from 4.3 to 5.5 (Fig. 1), which significantly reduced the SPI solid content in the solution. Therefore, the adhesives had a minimum viscosity at this pH range. As pH was either reduced to lower than 4.3 or increased to higher than 5.5, the precipitates started to dissolve, and hence, the viscosity increased. However, the SPI became partly denatured at pH 10 (Table I) due to breakage of hydrogen bonding, which is one of the major forces to stabilize protein structure. After denaturation, the soy protein subunits might have disassociated from each other, and smaller molecules were expected. Therefore, viscosity decreased again.

The viscosity of the PAE-modified SPI adhesives was also dependent on the PAE concentration (Table II). The adhesive with 5% PAE had the highest viscosity at pH 7.1. Most SPI molecules were still soluble at lower PAE concentrations, and the PAE molecules bound to SPI acted as physical crosslinking agents (Fig. 3), which increased the viscosity of the SPI solution. At higher PAE contents, however, SPI precipitated significantly at pH 7.1, as shown in Figure 1, and hence, the SPI content in the solution was reduced greatly, which consequently reduced the viscosity.

Adhesion strength

Shear-strength testing is a widely used method for the estimation of adhesion performance. The soaked-dried shear strength and wet shear strength were used as a measure of water resistance. Figure 5 shows

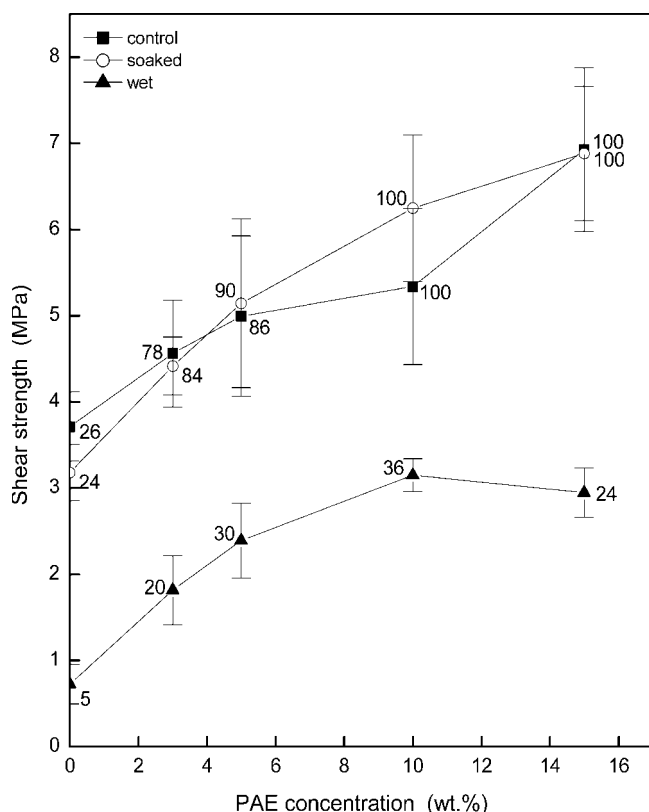


Figure 5 Effects of PAE concentration on the shear strengths of cherry plywood (pH = 7.1) bonded with the PAE-modified SPI adhesives pressed at 170°C and 1.4 MPa for 5 min: (■) dry, (○) soaked-dried, and (▲) wet shear strength. The data beside the symbol indicate the average percentage of CFW.

the shear strengths of the PAE-modified SPI adhesives at pH 7.1 was affected by PAE concentration. The adhesive shear strength increased sharply at first as the PAE concentration increased and then either increased slightly or leveled off (Fig. 5). The soaked-dried shear strength was not significantly different from the dry shear strength, which indicated that all bond forces were recovered after drying. The wet shear strength was about 50% lower than the dry adhesive strength (Fig. 5). The average percentages of cohesive failure within wood (CFW) are also presented in Figure 5. The unmodified SPI adhesive had very low CFW percentages, whereas the 10%- or 15%-PAE-modified SPI had 100% CFW for both the dry and soaked-dried shear strengths (Fig. 5). The wet shear strength of the 10% PAE-modified SPI adhesives gave 36% CFW. Therefore, the PAE modification greatly improved the performance of the SPI adhesives.

pH played an important role in controlling the performance of the SPI adhesives (Fig. 6). The adhesive shear strengths increased greatly as pH increased to 5.5 and then decreased sharply as pH further increased. The percentage of CFW had the same trends

against pH. Interestingly, even the wet shear strength reached a high value of 3.9 MPa with 72% CFW for the cherry plywood bonded with the 5%-PAE-modified SPI adhesive at a pH of 5.5.

PAE formed a complex with the SPI through ionic interactions at room temperature. Because both the PAE and SPI were macromolecules and had multi-functional groups, the complexation interactions could act as a physical crosslinks between PAE and SPI. Such complexation interactions still existed after the hot-press process, which should have been the main reason for the improvement of the adhesion strength and water resistance. PAE has a reactive azetidinium group, which is a four-member ring. The azetidinium group is not stable and can react with groups with active hydrogen.^{20–23} It has been proposed that the azetidinium group could react with primary and secondary amines and carboxyl groups at an elevated temperature (Fig. 7).^{19–23} However, this might not have been the case in our studies because Figure 8 shows that these chemical reactions occurred at higher temperature. The reaction peak temperature was 210°C for the adhesive in slurry form, and the reaction temperature shifted to 220°C for the adhesive dried in the oven (moisture content = 6.7%),

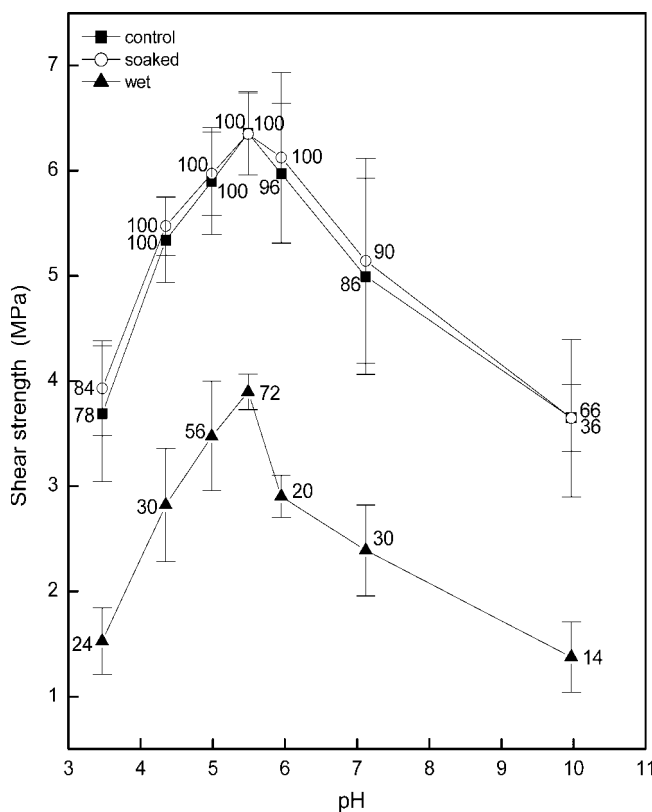


Figure 6 Effects of pH on the shear strengths of cherry plywood bonded with 5 wt % PAE-modified SPI adhesives pressed at 170°C and 1.4 MPa for 5 min: (■) dry, (○) soaked-dried, and (▲) wet shear strength. The data beside the symbol indicate the average percentage of CFW.

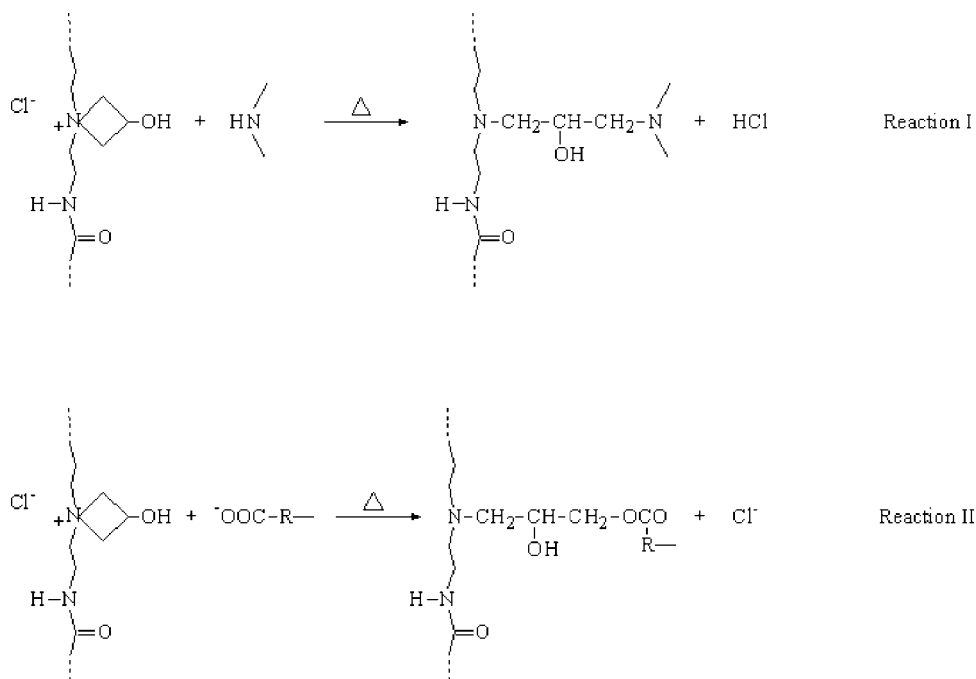


Figure 7 Schematic diagram of the chemical reactions between the azetidinium group of PAE and the primary and secondary amines and carboxyl group.

which was above the hot-press temperature. Treatment of the oven-dried sample in the hot press at 170°C and 1.4 MPa for 5 min reduced the reaction temperature by 3°C and the reaction enthalpy by

2.8%. The other peaks in Figure 8 were due to the denaturation of the SPI components. The complexation interaction had two main functions: (1) it acted as crosslinking between the PAE and SPI to form an in-

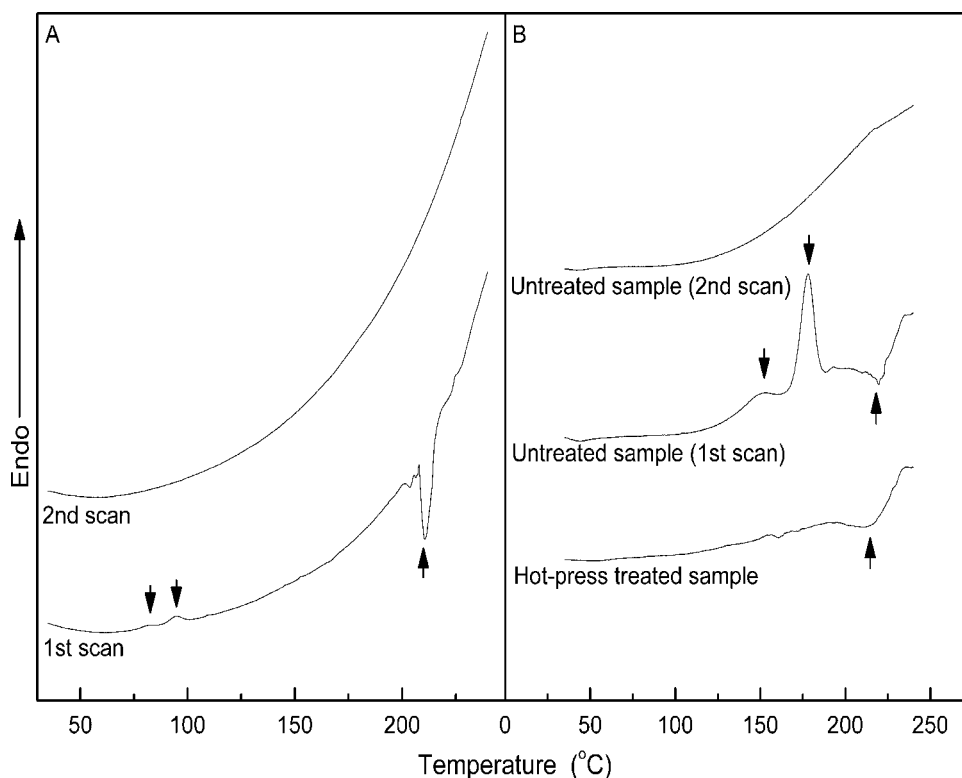


Figure 8 DSC thermographs of 15 wt % PAE-modified SPI adhesives in the (A) slurry state (moisture content = 89.1%) and (B) solid state (moisture content = 6.7%).

TABLE III
Comparison of the Adhesion Properties Among the Unmodified, 5% PAE-modified SPI Adhesives, and the Commercial Plywood Adhesives

pH	Adhesion strength (MPa)			
	Dry	Soaked-dry	Wet	Boiling
Unmodified SPI adhesive				
7.1	3.71 ± 0.40	3.18 ± 0.33	0.73 ± 0.23	0.31
	CFW 26%	CFW 24%	CFW 5%	80% Del
4.5	5.36 ± 0.21	4.83 ± 0.38	2.84 ± 0.22	1.79 ± 0.32
	CFW 100%	CFW 100%	CFW 50%	CFW 50%
5% PAE-modified SPI adhesive				
7.1	4.99 ± 0.93	5.14 ± 0.98	2.39 ± 0.43	0.64 ± 0.46
	CFW 86%	CFW 90%	CFW 30%	60% Del
5.5	6.36 ± 0.40	6.35 ± 0.39	3.90 ± 0.17	2.60 ± 0.37
	CFW 100%	CFW 100%	CFW 72%	CFW 64%
Commercial adhesives				
Urea-formaldehyde	5.00 ± 0.54	4.54 ± 0.49	3.46 ± 0.54	
	CFW 99%	CFW 96%	CFW 62%	100% Del
Phenol-formaldehyde	6.20 ± 0.47	6.59 ± 0.27	5.00 ± 0.35	3.59 ± 0.40
	CFW 100%	CFW 100%	CFW 96%	CFW 78%

CFW, cohesive failure within wood; Del, delaminated

soluble three-dimensional network, which improved the strength and water resistance of the adhesive itself and (2) the complexation interactions and such cross-linkages formed during reaction reduced the penetration of water into the interfacial layer between the wood and the adhesive. It was, therefore, understandable that the adhesion properties increased as the PAE concentration increased up to certain level. However, very high PAE content would have interfered with the interactions between the SPI and wood substrate, and hence, the adhesion properties leveled off or increased slightly at the PAE concentrations of 10% or above (Fig. 5).

Unmodified SPI adhesive²⁹ had a maximum adhesion strength and water resistance at its pI (i.e., pH 4.5, Table III). This was attributed to the special structure and conformation of SPI at its pI.²⁴ The value for maximum adhesive strength (or pI) shifted to pH 5.5 for the 5%-PAE-modified SPI adhesives (Fig. 6). The high dependence on pH of the ionic complexation interactions (Figs. 1–3) and the resulting special structure/conformation of the complexes should have played a key role in this shift. The complexation interactions were greatly enhanced at pH 5.5, as shown by the peak in Figure 1. The PAE-modified SPI also had the lowest net charge at pH 5.5, which greatly reduced the water resistance.

Table III compares the adhesion properties between the unmodified and the 5%-PAE-modified SPI adhesives. The unmodified SPI adhesive had lower strength and water resistance. The PAE modification improved the adhesion properties, and the change of pH to 5.5 further enhanced the adhesion performance. The 5%-PAE-modified SPI adhesive at pH 7.1 still had

a low water resistance, shown especially by the boiling test results. Changing the pH to 5.5 greatly improved the water resistance of the PAE-modified SPI adhesive, although the strengths were still lower compared to commercial phenol–formaldehyde (PF) plywood adhesives, which had a boiling shear strength of 3.6 MPa and a CFW of 78%.²⁹

Comparisons of the adhesion properties between the SPI adhesives and commercial urea–formaldehyde (UF) and PF plywood adhesives are given in Table III. The 5%-PAE-modified SPI adhesive had a much superior performance to the UF adhesive. Compared with PF resin, the 5%-PAE-modified SPI adhesive had similar dry and soaked adhesion strength but slightly lower wet and boiling strengths. From an economic point of view, current food-grade SPI is about \$1 per pound. However, the cost of SPI adhesives is comparable to UF and PF adhesives because the solid concentration of SPI adhesive is about 11%. The cost for SPI adhesive should be even lower if industrial-grade SPI is used for adhesive applications.

CONCLUSIONS

PAE and SPI molecules formed reversible complexes at room temperature through ionic interactions between the cationic azetidinium group of PAE and the anionic carboxyl group of SPI. The PAE/SPI complex disassociated at basic conditions (pH > 9) or extremely acidic conditions (pH < 4). The formation of the complex stabilized the SPI structure and increased its T_d and ΔH_d . The PAE modification

greatly improved the adhesion properties of the soy-protein-based adhesives. The complexation interaction occurring at or near the isoelectric pH was the main reason for this improvement in adhesion properties.

References

1. Freedom Group. Adhesives to 2004: Market Size, Market Share, Demand Forecast, and Sales. <http://www.freedomgroup.com/adhesives.html> (accessed July 2004).
2. Kumar, R.; Choudhary, V.; Mishra, S.; Varma, I. K.; Mattiason, B. *Ind Crops Prod* 2002, 16, 155.
3. Mohanty, A. K.; Liu, W.; Tummala, P.; Drzal, L. T.; Misra, M.; Narayan, R. In *Natural Fibers, Biopolymers, and Biocomposites*; Mohanty, A. K.; Misra, M.; Drzal, L. T., Eds.; Taylor & Francis: New York, 2005; Chapter 22.
4. Sun, X. S. In *Biobased Polymers and Composites*; Wool, R.; Sun, X. S., Eds.; Elsevier: Oxford, 2005; Chapter 10.
5. Energy Information Administration, U.S. Department of Energy. *Petroleum 1996: Issues and Trends*. <http://tonto.eia.doe.gov/FTPROOT/petroleum/061596.pdf> (accessed June 2006).
6. U.S. Environmental Protection Agency. Sources of Indoor Air Pollution: Formaldehyde. <http://www.epa.gov/iaq/formaldehyde.html> (accessed June, 2006).
7. U.S. Environmental Protection Agency. Sources of Indoor Air Pollution: Organic Gases (Volatile Organic Compounds—VOCs). <http://www.epa.gov/iaq/voc.html> (accessed June 2006).
8. National Institute of Environmental Health Sciences. New Carpet Allergy. <http://www.niehs.nih.gov/external/faq/carpet.htm> (accessed June 2006).
9. Kalapathy, U.; Hettiarachchy, N. S.; Myers, D.; Hanna, M. A. *J Am Oil Chem Soc* 1995, 72, 507.
10. Hettiarachchy, N. S.; Kalapathy, U.; Myers, D. *J Am Oil Chem Soc* 1995, 72, 1461.
11. Kalapathy, U.; Hettiarachchy, N. S.; Myers, D.; Rhee, K. C. *J Am Oil Chem Soc* 1996, 73, 1063.
12. Sun, S. X.; Bian, K. *J Am Oil Chem Soc* 1999, 76, 977.
13. Huang, W.; Sun, X. *J Am Oil Chem Soc* 2000, 77, 101.
14. Huang, W.; Sun, X. *J Am Oil Chem Soc* 2000, 77, 705.
15. Rogers, J.; Geng, X.; Li, K. *Wood Fiber Sci* 2004, 36, 186.
16. Mo, X.; Sun, X.; Wang, D. *J Am Oil Chem Soc* 2004, 81, 395.
17. Zhong, Z.; Sun, X. S.; Fang, X.; Ratto, J. A. *J Adhes Sci Technol* 2001, 15, 1417.
18. Zhong, Z.; Sun, X. S.; Fang, X.; Ratto, J. A. *Int J Adhes Adhes* 2002, 22, 267.
19. Li, K.; Peshkova, S.; Geng, X. *J Am Oil Chem Soc* 2004, 81, 487.
20. Espy, H. H. In *Wet-Strength Resins and Their Application*; Chan, L. L., Ed.; TAPPI: Atlanta, GA, 1994; Chapter 2.
21. Dunlop-Jones, N. In *Paper Chemistry*; Roberts, J. C., Ed.; Blackie: New York, 1996; Chapter 7.
22. Espy, H. H.; Rave, T. W. *Tappi J* 1988, 71, 133.
23. Espy, H. H. *Tappi J* 1995, 78, 90.
24. *Annual Book of ASTM Standards*; American Society for Testing and Materials: Philadelphia, 1995; Vol. 15.06, ASTM D 2339.
25. *Annual Book of ASTM Standards*; American Society for Testing and Materials: Philadelphia, 1992; Vol. 15.06, ASTM D 1183.
26. *Annual Book of ASTM Standards*; American Society for Testing and Materials: West Conshohocken, PA, 2000; Vol. 15.06, ASTM D 1151.
27. *Annual Book of ASTM Standards*; American Society for Testing and Materials: Philadelphia, 1994; Vol. 15.06, ASTM D 5572.
28. Nielsen, N. C. In *New Protein Food*; Altschul, A. M., Ed.; Academic: New York, 1985; Vol. 5.
29. Sun, X. S.; Wang, D.; Zhong, Z.; Yang, G. U.S. Pat. Appl. 60/533,780 (2004).