Improving Water Resistance of Soy-Protein Wood Adhesive by Using Hydrophilic Additives

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Soy protein adhesives are good candidates for the replacement of formaldehyde-based adhesives due to environmental concerns. However, poor water resistance has limited their application. This study was conducted to improve the water resistance of a soy-protein adhesive intended for plywood by polyethylene glycol (PEG) with different molecular weights. Ethylene glycol (EG), diethylene glycol (DEG), 400-, 2000-, and 10000-dalton polyethylene glycols were used as additives to soy protein isolate (SPI). The hydrogen bonding interaction, thermal properties, wettabilities on poplar veneer, and adhesion properties of the blended adhesives were investigated. Results showed that improving the wettability and intermolecular hydrogen bonding, induced by ethylene glycol, increased the wet adhesion strength by 30%. Higher-molecular weight polyethylene glycol imposed a decrease in adhesion due to its poor water resistance. Based on the present results, it is proposed to improve the water resistance of soy adhesives by introducing hydrophilic polyols, which also could simultaneously improve surface wetting and wet adhesion.

Keywords: Soy-protein; Poly(ethylene glycol); Adhesion; Hydrogen bonding; Adhesive

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INTRODUCTION

With increasing concern of environmental pollution from petroleum-based chemicals, biomaterials have attracted much interest from researchers and industries for replacement of petroleum-based materials (Hubbell 1995; Ringler and Schulz 2003; Ladet *et al.* 2008). In the area of wood-based composites manufacturing, urea formaldehyde (Wang and Pizzi 1997a,b), phenolic aldehyde (Peshkova and Li 2003), and melamine (Fan *et al.* 2011) resins, which are petrochemical and formaldehyde based, are commonly used as adhesives. For environmental concerns, research interests on wood adhesive have shifted to formaldehyde-free natural materials such as lignin (Pizzi 2006; Amaral-Labat *et al.* 2008), tannin (Li *et al.* 2004; Vazquez *et al.* 2006), protein (Kalapathy *et al.* 1995; Liu and Li 2004), and others (Khan *et al.* 2004; Li and Geng 2004; Geng and Li 2006). Soy protein, extracted from widely-grown soybean, is one of the most studied materials among them, especially for plywood manufacturing. In the last twenty years, soy protein has been modified in many different ways as a plywood adhesive, as it offers excellent dry adhesive strength and low cost (Li *et al.* 2009; Sheng 2009; Ciannamea *et al.* 2010; Liu *et al.* 2010; Zhang *et al.* 2013). However, high viscosity, low solids content, and poor water resistance limit the application of soy protein adhesives, and many studies have been carried out to solve these problems.

Most researchers use modifying agents to denaturalize the higher order structure of soy protein and make it water resistant. Sun's group used alkaline treatment (Sun and

Bian 1999), urea (Huang and Sun 2000), and sodium dodecyl sulfate (Zhong and Sun 2001) separately to modify and isolate soy protein. A significant improvement in wet shear strength was observed with only a small amount of the modifying agent. Some researchers chemically changed the soy protein structure by grafting or copolymerization to make it hydrophobic. Liu and Li (2007) found that a combination of maleic-anhydride-grafted soy protein and polyethylenimine dramatically increased the strength and water resistance of the resulting wood composite. Another method of applying soy protein as wood adhesive was to decompose it by heating or by using a strong acid/base, followed by a crossing linking reaction with synthetic resins. The method would be beneficial for reducing the viscosity and can be applied for particleboard manufacturing. Amaral-Labat *et al.* (2008) proposed an environmentally-friendly soy flour-based resin by cross-linking glyoxalated soy flour and a tannin mixture using polymeric isocyanate as the cross-linking agent. The particleboard made from the resin exhibited a satisfactory result relative to the relevant standard specifications for interior wood board.

Liu *et al.* (2010) proposed an effective way by introducing nanocrystalline calcium carbonate into the soy protein isolate. The resulted adhesive would penetrate into the wood lumens to form interlocking links and various ionic bonding interactions formed between the wood and soy adhesive to present a great improvement on water-resistance and bonding strength. The work proposed a new method to improve the water resistance of soy adhesive by ionic bonding interaction.

These chemical modifications of soy adhesives are based on the chemical reactions related to amides and amino groups. Recent research performed on protein-based materials, introduced polyol with different molecular weight, especially PEGs, having various effects on the structural and mechanical properties of the material (Vivares *et al.* 2002; Wang and Annunziata 2007; Dumetz *et al.* 2008; Ngadi *et al.* 2009; Ji *et al.* 2012). However, there is little information on the effects of polyol molecular size on adhesion properties of soy protein.

This study was carried out to evaluate the adhesion properties of soy adhesives prepared from soy protein isolate blended with PEGs with different molecular weights. The hydrogen bonding interaction, thermal properties, and surface wettabilities on poplar veneer for the blended adhesives were also studied. The complex relationship between the adhesive properties and plywood shear strength was presented. This study is helpful in understanding the relationship between the molecular sizes of the polyol additive and the adhesion properties of soy adhesive. This study also presents an efficient method to adjust the water resistance by introducing polyols with different molecular weights.

EXPERIMENTAL

Materials

Poplar (*Populus* spp.) veneers were provided by Anhui Tiankang Timber Co. Ltd. (China). The veneer samples were conditioned at 25 °C and a 65 ± 5% relative humidity (RH) to a moisture content of 9%. All samples were kept in a sealed box to balance the moisture content.

Commercial soy protein isolate (SPI), purchased from Harbin Hi-Tech Soybean Food Co., Ltd. (China), with protein content ≥ 88%, moisture content ≤ 7.0%, and ash content ≤ 6.5%. Ethylene glycol, diethylene glycol, poly(ethylene glycol) 400, poly(ethylene glycol) 2000, poly(ethylene glycol) 10,000, and sodium hydroxide of analytic grade (labeled EG, DEG, PEG400, PEG2000, PEG10000, and NaOH, respectively) were purchased from Nanjing Chemical Reagent Co., Ltd. (China), and used as received.

Methods

Preparation and characterization of PEG-modified soy protein (SPI-PEG) adhesives

In a reaction bottle equipped with a mechanical stirrer and thermometer, 90 g of water, 10 g of SPI, and 3 g of modifying agent (EG, DEG, PEG400, PEG2000, or PEG10000, labeled SPI-EG, SPI-DEG, SPI-PEG400, SPI-PEG2000, and SPI-PEG10000, respectively) were added at 25 °C, and the mixture was adjusted to a pH of 10 by addition of 20 wt% NaOH. The reaction mixtures were then heated to 70 °C for 20 min. Finally, the resultant mixture was cooled to room temperature, obtaining a homogeneous yellow suspension, and used as the SPI-PEG adhesive.

For a comparison, unmodified soy protein adhesive (SPI), used as the control, was prepared in accordance with the above procedure without the addition of the modifying agent.

Chemical and physical characterization of unheated and heated SPI-PEG adhesive

The modified SPI-PEGs was dried at 35 °C with air atmosphere for two days and then further dried in a vacuum at 25 °C for another day. A light yellow solid was obtained as the unheated adhesive powder. It was then pressed at 160 °C with a pressure of 1.0 MPa for 5 min to obtain the heated SPI-PEG adhesive films.

Both unheated and heated SPI-PEG adhesives were vacuum-dried at 25 °C for 24 h and then ground into powder before they were pelletized with KBr for Fourier transform infrared (FTIR) spectroscopy measurements. The FTIR spectra were recorded on an FTIR spectrometer (Nicolet 380 FT-IR; Thermo Fisher Scientific Inc., USA) over a wavenumber range of 4000 to 400 cm^{-1}.

Thermal gravity (TG) analysis was conducted on a TG 209 F3 Tarsus provided by Netzsch Co. Ltd. (USA). Approximately 5 mg of unheated SPI-PEG sample was measured in a nitrogen atmosphere at a flow rate of 30 mL•min^{-1}. The samples were heated at a rate of 10 °C min^{-1} from 35 to 700 °C in an alumina sample pan.

Wettability of SPI-PEGs on a poplar veneer surface

Wettability analysis of SPI-PEGs on a poplar veneer surface was conducted by measuring the contact angle. The contact angle was defined as the angle through the liquid phase formed between the surface of a solid and the line tangent to the droplet radius from the point of contact with the solid (Ayrilmis *et al.* 2009). To determine the contact angle, drops of SPI-PEG adhesive were uniformly dispersed on the veneer (4 mm × 10 mm in size), which were previously conditioned to a moisture content of 9%. To minimize the influence of surface roughness, the tight sides of the veneers were chosen in all tests, and were sanded with 100 grit sandpaper before use. The contact angle was tested by an Attension Theta Optical Tensiometer (Biolin Scientific, Sweden), and measured every 5 s for 100 s after it was dropped on the veneer surface. The contact angle was automatically measured by the Attension software provided by the tensiometer manufacturer. Tests were repeated at least three times. When a drop of liquid was placed on the surface of veneer, a contact angle was formed immediately at the solid and liquid interface, and defined as the "initial contact angle". When the rate of change of the contact angle reached a constant, a well-defined contact angle value was determined, and was defined as the "equilibrium contact angle" (Nussbaum 1999).

Viscosity of the adhesives were test on NDJ-79 rotational viscometer provided by Shanghai Changji Instruments Co., Ltd. at 25 °C.

Plywood manufacture

Poplar veneer, with a thickness of 0.15 cm and a moisture content of 9% from which three-layer-plywood panels were produced, was cut into boards with a dimension of 20.0 cm × 20.0 cm. The SPI-PEG adhesive was spread on the veneer at a dry weight of 4.0 mg/cm^2. Hot pressing time and pressure were 4.5 min and 1.0 MPa, respectively, at 160 °C in the manufacturing of the panels.

After hot-pressing, panels were stored in an ambient environment for at least 24 h before being tested. For each condition, three replicates were produced.

Shear strength of plywood

Prior to the mechanical test, plywood panels were conditioned at 25 °C and 65 ± 5% RH until equilibrium moisture content was reached. The wet shear strength of the panel was characterized according to the Chinese National Standard for Plywood (GB/T 9846.3 2004). After soaked in water at 63 ± 3 °C for 3 h, delamination of all panels was inspected, and then the panels were cooled to 25 ± 5 °C. The shear strength properties of the panels were tested on a mechanical testing machine (SANS; Shenzhen, China) when they were still wet. The shearing speed was 1.0 mm/min. At least 30 samples were tested for each group.

RESULTS AND DISCUSSION

FTIR Analysis

Hydrophilic groups, *e.g.*, hydroxyls, amines, and amides, greatly affect the water resistance of soy adhesives. Hence, it is essential to investigate the effect of poly(ethylene glycol) on the hydrophilic structures of soy protein by the infrared spectrum.

The FTIR spectra of unheated SPI-PEGs are presented in Fig. 1. The absorption maximum at 3270 cm^{-1} in the SPI curve attributes to the stretching of N-H from the amide (Venkatachalapathi *et al*. 1987). The sharp absorption maxima at 1627 cm^{-1}, 1520 cm^{-1}, and 1234 cm^{-1} could be attributed respectively to the amide I (C=O stretching), amide II (CN stretching, NH bending), and amide III (CN stretching, NH bending) (Wang and Wu 2012; Shen *et al.* 2013; He *et al.* 2014; Wang *et al*. 2014). The bands at 1442 cm^{-1} and 1388 cm^{-1} could be assigned to the amino acid side chain vibrations (He *et al.* 2014). The absorptions from 1000 cm^{-1} to 1140 cm^{-1} were attributed to the stretching of the ether bond in PEGs, and the differences originate from the different molecular weights. When PEGs with molecular weight lower than 400 were blended with SPI, the 3270 cm^{-1} absorption intensity increased, due to the introduction of the hydroxyl groups from the PEGs (Kolhe and Kannan 2003). When the molecular weight of the PEGs was over 2000, the stretching absorption maximum of the active hydrogens shifted from 3270 cm^{-1} to 3419 cm^{-1}. A similar case was also observed for the carbonyl stretching absorption of amide I. When blended with EG, DEG, and PEG400, the amide I absorption at 1627 cm^{-1} stayed unchanged. When molecular weight of PEG increased to over 2000, the amide I absorption shifted to 1652 cm^{-1}. As the formation of hydrogen bonding could average the electron cloud density, corresponding stretching would move to lower frequency. The blue shifts of both the stretching vibrations may reflect weakened hydrogen bonding between hydrogen and carbonyl after introducing of PEG2000 and larger blenders. For SPI, intramolecular hydrogen bonding acts to form a helix and a folding structure. When blended with small molecular PEGs, the PEGs may penetrate into the protein matrix, and hydrogen bondings were formed between active hydrogens (from N-H and O-H) and amide from protein (Gellman *et al.* 1991; Hamley and Krysmann 2008).

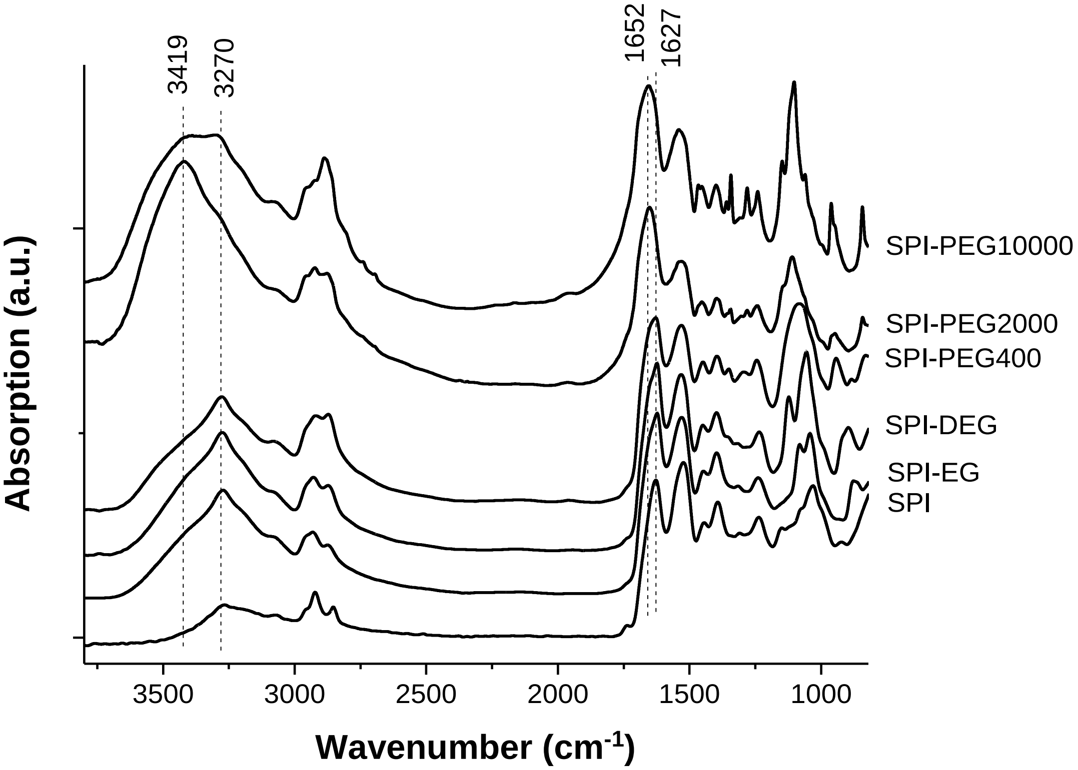

Fig. 1. Comparison of FTIR for SPI-PEGs before heating

The infrared spectra after the specimens were heated at 160 °C for 5 min are illustrated in Fig. 2. The wavenumbers of both hydrogen-bonded and unbonded active hydrogen (from O-H and N-H) shifted slightly from 3270 cm^{-1} and 3419 cm^{-1} to 3274 cm^{-1} and 3422 cm^{-1}. The wavenumbers of the carbonyl groups were significantly shifted to smaller wavenumbers, from 1627 cm^{-1} and 1652 cm^{-1} to 1620 cm^{-1} and 1643 cm^{-1} for both hydrogen-bonded and unbonded amide I. The red shift of the amide I indicates an enhanced intermolecular interaction after heating, while the blue shift of active hydrogen indicates a weakened interaction. The slight shifts of the absorptions may be attributed to the denaturation of protein. For the SPI and SPI-PEG400 samples, the stretching absorptions of active hydrogen at 3270 cm^{-1} shifted to 3422 cm^{-1}, and the amide I at 1627 cm^{-1} shifted to 1643 cm^{-1}. The shifts of the both absorptions could be attributed to the conversion from hydrogen-bonded state to unbonded state, and are in accordance with each other. For all the other SPI-PEG samples, the hydrogen bonding behavior stayed the same throughout the heating process. After heating, SPI-EG and SPI-DEG showed strong hydrogen bonding interaction, while SPI-PEG2000 and SPI-PEG10000 showed no conjugation between the hydroxyl and carbonyl groups.

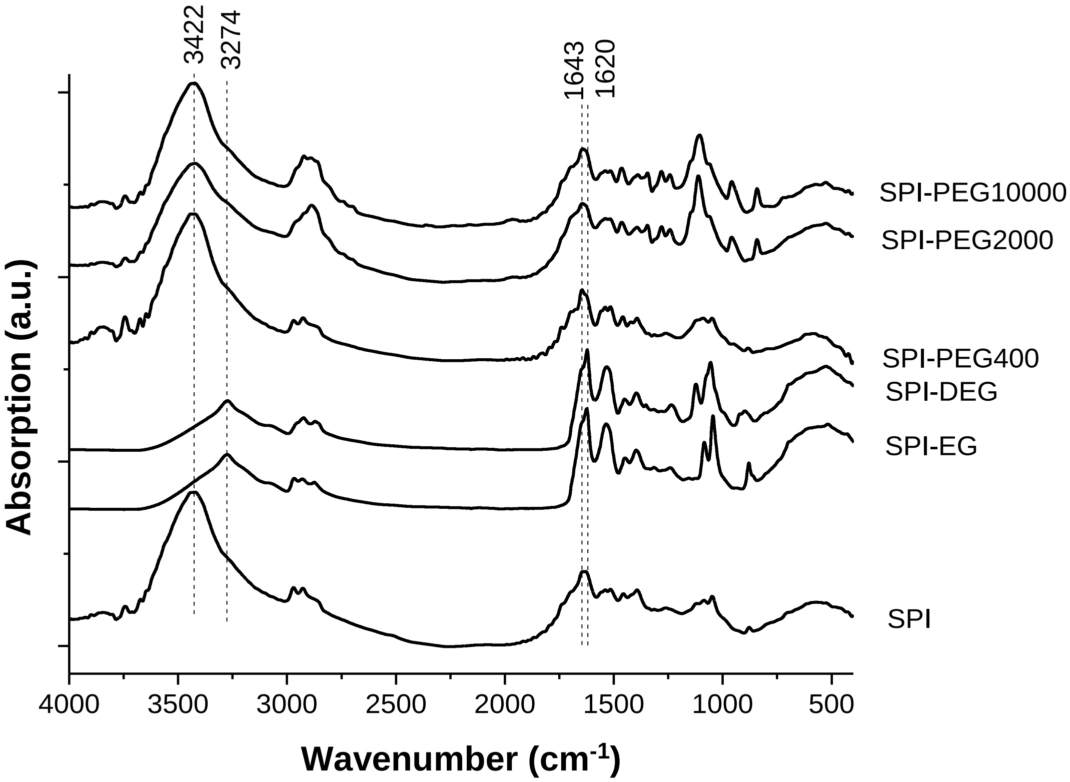

Fig. 2. Comparison of FTIR for SPI-PEGs after heating

From the comparison of the infrared spectra of the unheated and heated SPI samples, active hydrogen and amide I were converted from a hydrogen-bonded state to an un-hydrogen-bonded state during heating. The conversion made the material more water-sensitive, due to the hydrophilicity property of the hydroxyl, amino, and carbonyl groups. This transition indicates that the heating process would break down the hydrogen bonding structure. By introducing low molecular weight polyols (like EG, DEG, and PEG400), hydrogen bonding formed between the active hydrogen (*e.g.*, hydroxyl, amine and *etc.*) and carbonyl group. However, hydrogen bonding formed in SPI-PEG400 is not stable during heating, and disappeared after heating at 160 °C for 5 min. A further increase in molecular weight of polyols (like PEG2000 and PEG10000) would make it difficult for large molecules interpenetrating into the protein matrix, and not be beneficial for the formation of hydrogen bonding.

Thermal Gravity Analysis

For further investigation, thermal gravity was also conducted on the unheated SPI-PEGs. Figure 3 shows the derivative thermal gravity (DTG) data of the SPI-PEGs. Three peaks in DTG illustrate the three stages of weight losses. The weight losses could be attributed to: the one at 50 to 120 °C as evaporation of water, the one at 304 to 307 °C as the decomposition of protein, and the one that varies from 245 to 408 °C as the evaporation or decomposition of PEGs. Boiling points for ethylene glycol and diethylene glycol are 197 °C and 245 °C, respectively. A weight loss peak at 245 °C, which could be attributed to evaporation of diethylene glycol, is clearly presented for SPI-DEG in Fig. 3. The weight loss at 377, 397, and 408 °C comes from the decomposition of the PEGs, respectively for SPI-PEG400, SPI-PEG2000, and SPI-PEG10000. However, the evaporation of ethylene glycol, which should be a sharp weight loss peak around 197 °C, could not be observed from the curve of SPI-EG. A continuous weight loss started from 140 °C and merged into the decomposition of protein for the SPI-EG sample.

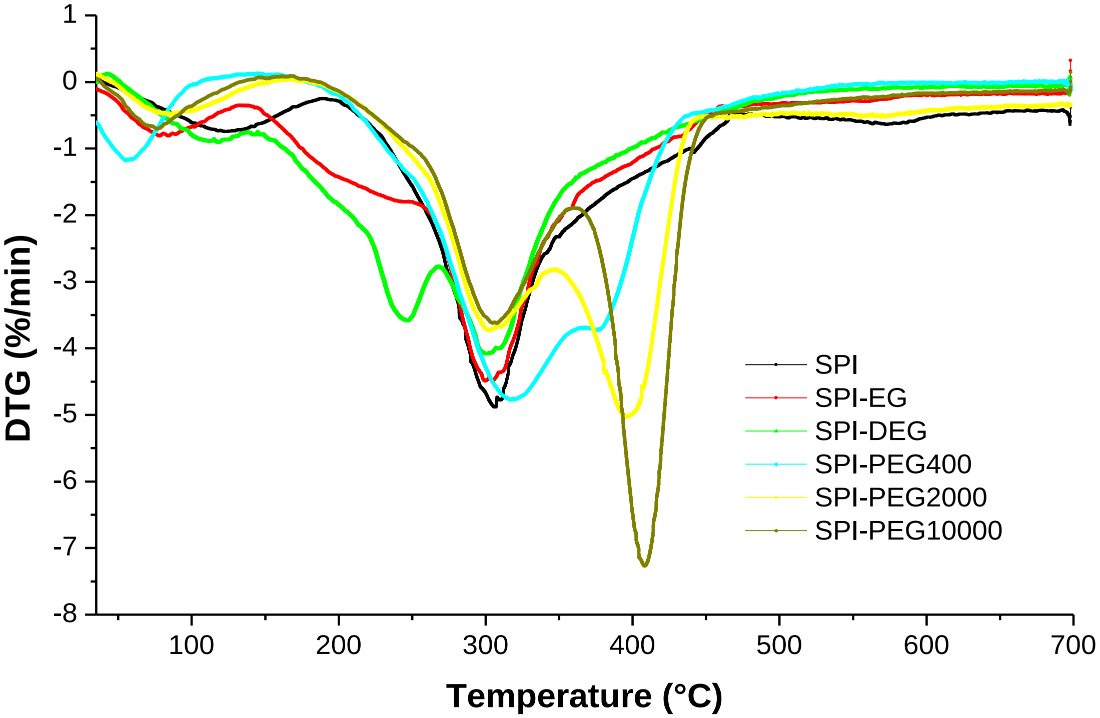

Fig. 3. DTG curves of the SPI-PEGs ranging from 35 to 700 °C at a heating rate of 10 °C·min^{-1}

From the infrared spectra of SPI before and after heating, hydrogen bonding decomposition could be clearly seen. As no polyol was introduced into the SPI sample, the hydrogen bonding formed before heating should be contributed by the intramolecular interaction inside the protein (mainly results in formation of N-H···O=C). The heating treatment made the hydrogen-bonding-induced self-assembly of protein difficult. However, the hydrogen bonding interaction was also detected for SPI-EG and SPI-DEG after heating from the infrared spectra. It is suspected that this hydrogen bonding was contributed by the intermolecular interaction between the protein and the PEGs (mainly results in the formation of O-H···O=C). For the SPI-EG sample, no EG evaporation was observed from the DTG curve around its boiling point of 197 °C. Most EG molecules are strongly hydrogen-bonded with protein, and the formation of hydrogen bonding significantly increases the boiling point of EG. For the SPI-DEG sample, as the evaporation temperature of DEG observed in the DTG curves is in good accordance with its boiling point, the hydrogen bonding should be in a much smaller amount and have a weaker intensity than the one in the SPI-EG sample.

Wettability of SPI-PEGs on Poplar Veneer Surface

Contact angles are widely used for the analysis of surface properties (Owens and Wendt 1969; Gindl *et al.* 2001; Aydin 2004). In the application of adhesives, it is an indicator of the affinity of the glue (Liu *et al.* 2010).

Soy protein adhesives blended with PEGs of different molecular weights presented different wetting behavior on the veneer surface. When a drop of adhesive was placed, in the initial stage, a contact angle was formed at the solid and adhesive interface. Then the adhesive spread and penetrated into the veneer until an equilibrium angle was obtained. As shown in Fig. 4, the contact angle decreased as a function of wetting time. At the initial stage of wetting, the contact angle decreased rapidly. After about 15 seconds, the contact angle came to equilibrium. The equilibrium contact angle exhibits the adhesive wettability on the veneer surface. The smaller equilibrium angle exhibits better wettability. As presented in the inserted figure in Fig. 4, the equilibrium contact angle of SPI-EG was smaller than the SPI. With further increasing of PEG molecular weight, the equilibrium contact angle got larger. When the molecular weight of PEG reached 10000, the equilibrium angle reached a constant with a slight decrease.

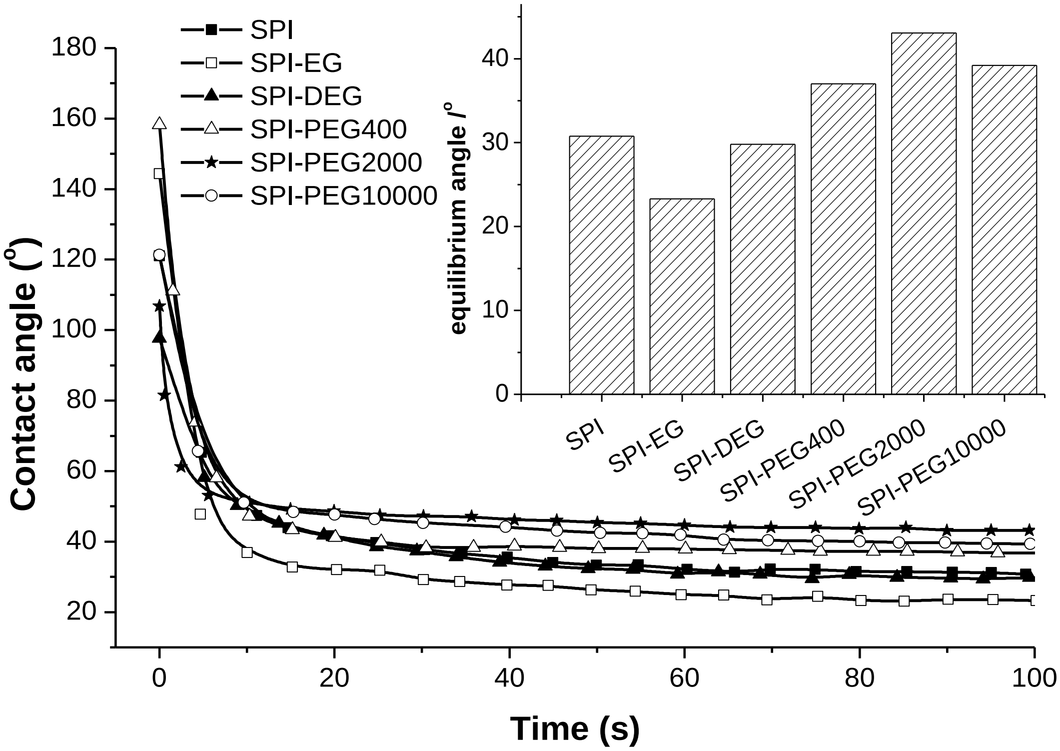

Fig. 4. The contact angle values of SPI-PEGs change as a function of wetting time. Inserted: comparison of the equilibrium values

Table 1. Viscosity of SPI-PEG Adhesives

	SPI	SPI-EG	SPI-DEG	SPI-PEG400	SPI-PEG2000	SPI-PEG10000
Viscosity (mPa·s)	400	220	320	330	320	350

Viscosity values have a great effect on the wettability of adhesive. As presented in Table 1, SPI exhibited the highest viscosity of 400 mPa·s among the samples. After blending with EG, the viscosity decreased to 220 mPa·s. Further increasing molecular weight to DEG, the viscosity increased to 320 mPa·s again. The trend of equilibrium contact angle change for small molecular weight (smaller than 400 dalton) is in good accord with the viscosity change. However, with further increasing the molecular weight of PEGs, the viscosity stayed almost the same around 320 to 350 mPa·s, which is different from the change of equilibrium contact angle.

Ethylene glycol is hydrophilic, with hydroxyl ends. The surface of poplar veneer is also hydrophilic with hydroxyl and carbonyl groups, which originated from cellulose, hemicellulose, and lignin. When drops of SPI-EG spread on the poplar veneer surface, hydrophilic interactions and low viscosity would be beneficial to the surface wetting. When the molecular weight of PEGs was increased, the mobility of the PEG chain decreased, and a decrease in wettability was observed. When the molecular weight of PEG was higher than 2000, the mobility of PEG was mostly stable, and the equilibrium angle stayed constant.

Plywood Shear Strength Evaluation

The molecular weight effects of PEG on the shear strength of the plywoods bonded with SPI-PEG adhesives, after all specimen soaked in 63 ± 3 °C water for 3 h, are shown in Fig. 5. The shear strength of SPI-EG was 1.3 times of the strength of the SPI adhesive. With increasing the molecular weight of PEGs to 400, the shear strength decreased gradually. Further increasing of the PEG molecular weight resulted in a slight improving in shear strength. The one-way analysis of variance (ANOVA) results revealed statistically significant differences in mean shear strength between different molecular weight of PEGs ($p<0.001$, F=25.906).

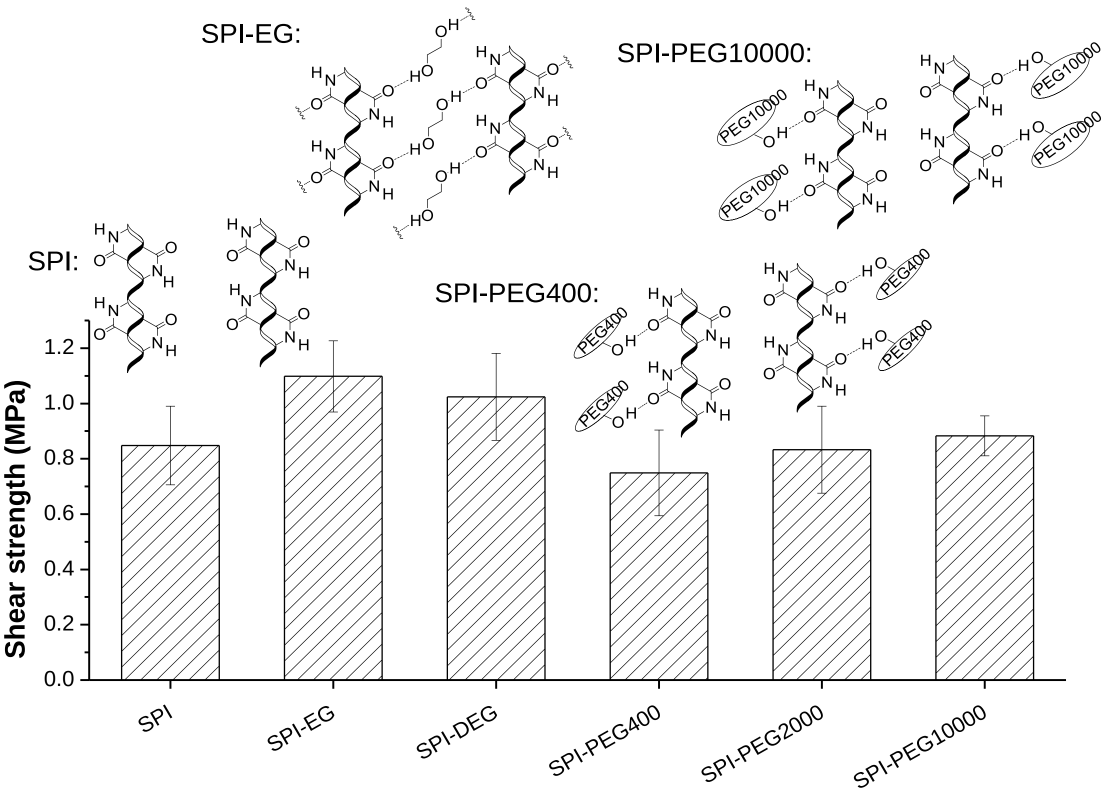

Fig. 5. Molecular weight effect of PEGs on the shear strength of plywoods bonded with SPI-PEG adhesives. All panels were treated according to GB/T 9846.3 2004. The schemes above represent the interaction between SPI and PEG after heating, where SPI, SPI-EG, SPI-PEG400, and SPI-PEG10000 are represented.

The significant increase in shear strength after the introduction of ethylene glycol could be explained by the formation of hydrogen bonding between the protein and ethylene glycol, as well as the better wetting behavior proved by the contact angle study. It is believed that the hydrophilic groups outside the polypeptide chain result in water-sensitivity of the soy protein adhesives (Liu *et al.* 2010). During heating, intramolecular hydrogen bonding is broken, hydrophilic amide is exposed in the protein matrix, as shown in the scheme of SPI in Fig. 5. By introducing EG into the protein matrix, hydrogen bonding, which is relatively stable, is formed between the carbonyl groups on amide and hydroxyl groups on ethylene glycol. In this process, the hydrogen bonded ethylene glycol acts as a new “cross-linking” point in the polypeptide network, as shown in the scheme of SPI-EG in Fig. 5. During TG analysis, most EG molecules had strong hydrogen bonding interaction with the protein and exhibited no independent evaporation at its boiling point, but evaporated with the decomposition of protein (as shown in Fig. 3). It was also proved from the infrared spectra, that before and after heating, significant hydrogen-bonding absorptions were observed. When soaked in warm water, the more “cross-linked” SPI-EG exhibits better water resistance and higher shear strength than SPI.

When increasing molecular weight of PEGs, larger molecular size and less hydroxyl group would be obtained. It would be difficult for PEGs to interpenetrate into the matrix of protein, especially for large PEGs. In this case, hydrogen bonding would only be formed between hydroxyl groups on PEGs and carbonyl groups outside the protein matrix (as shown in the scheme of SPI-PEG400 and SPI-PEG10000 in Fig. 5). The interaction between PEG and protein would be much weaker than SPI-EG. In the TG analysis, evaporation of DEG is in good accordance with its boiling point, which indicated this weak interaction could be easily destroyed at high temperatures. Before the heating of the SPI-PEG complex, hydrogen bonding would be preferentially formed for DEG and PEG400, due to their better mobility and hydrophilic interaction between hydroxyl and amide. As a result, hydrogen bonding could be observed for SPI-DEG and SPI-PEG400 (Fig. 1). With increasing molecular weight from PEG2000 to PEG10000, the hydroxyl groups provided by PEGs caused their mobility to decrease significantly. As a result, the proportion of unhydrogen-bonded active hydrogen exceeded the hydrogen-bonded one. After heating, the formation of the protein matrix excluded the PEG molecules and hydrogen bonding could only be formed between the hydroxyl of PEG and the carbonyl outside of the protein matrix, and thus, much less carbonyl could be provided by the protein. Consequently, even for SPI-PEG400, the unhydrogen-bonded active hydrogen exceeded the hydrogen-bonded one after heating (Fig. 2). Considering PEG chains are hydrophilic, when soaked in warm water, SPI-PEGs exhibited worse water resistance and possessed lower shear strength than SPI-EG. However, when the molecular weight of PEG is higher, the PEGs would provide a wider depletion zone for protein, and crystallization of protein would be beneficial as a consequence (Tanaka *et al.* 2003). The increased crystalline region explains the improvement in shear strength of SPI-PEG2000 and SPI-PEG10000 samples (Frihart 2010).

Wettability on a veneer surface also contributed to the shear strength. With the introduction of EG, wettability on the veneer surface improved and resulted in better adhesion. Further increasing of the molecular weight of PEG decreased the surface wetting, and provided a decreased shear strength.

CONCLUSIONS

1. The SPI-EG adhesive exhibits shear strength 1.3 times larger than SPI adhesive. Further increase in molecular weight of PEG decreases the shear strength. When PEG molecular weight exceeds 2000, the shear strength increases again with the molecular weight of PEG.
2. By introducing EG into SPI, the hydrogen bonding interaction formed inside the matrix of the heated protein, and it made the evaporation of EG difficult. Formation of intermolecular hydrogen bonding inside the protein matrix made SPI-EG adhesive-based plywood have better water resistance and higher shear strength.
3. By introducing PEGs with higher molecular weight into SPI, the hydrogen bonding interaction could only be formed between the hydroxyl of PEG and amide outside the heated protein matrix, due to the very large molecular size of PEG. Hydrophilicity and molecular weight of PEG influences the water resistance of the corresponding plywood. SPI-PEG400 represented poor water resistance and shear strength, while SPI-PEG2000 and SPI-PEG10000 were better.
4. Introduction of EG made the wettability of the protein on poplar veneer better than SPI adhesive. Further increasing of the molecular weight of PEG would reduce the surface wetting for the molecular mobility issue. When the PEG molecule was larger than 2000, the wettability only changed slightly.

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