Preparation of Wood Adhesives Based on Soybean Meal Modified with PEGDA as a Crosslinker and Viscosity Reducer

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To increase the water resistance and reduce the viscosity of soybean meal (SM)-based non-formaldehyde wood adhesives, polyethyleneglycol diacrylate (PEGDA) used as crosslinker and viscosity reducer was introduced into the SM adhesive system. The apparent viscosity was evaluated by rheological measurements; gel content and water absorption of adhesives, the wet shear strength of plywood bonded with these modified adhesives were tested to evaluate their water resistance. In addition, the crosslink structures of modified adhesives were characterized by Fourier transform infrared (FTIR) spectroscopy and solid-state ^{13}C NMR analysis. The results indicated that all of the SM adhesives were pseudoplastic fluids with the property of shear-thinning. The viscosity of modified SM adhesives effectively decreased by 35% compared with the addition of PEGDA, and the wet shear strength of their bonded plywood increased; the wet shear strength of plywood bonded with 4% PEGDA-modified SM adhesive increased 114.2% compared to SM adhesive. FTIR spectroscopy and solid-state ^{13}C NMR analysis demonstrated that the crosslinking reaction of the PEGDA occurred successfully during the curing process of PEGDA modified SM adhesive, and no crosslinking reaction between the PEGDA and soy meal adhesive appeared to have occurred. Interpenetrating networks (IPNs) might be formed between the cured PEGDA and SM adhesive system.

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INTRODUCTION

Formaldehyde-based adhesives have been widely used in the wood processing industry because of their good bonding strength, water resistance, heat resistance, and low cost (Boquillon *et al.* 2004; Kamoun *et al.* 2003). However, in recent years, limited petroleum resources and the pollution caused by formaldehyde-based adhesives have spurred many efforts to develop environmentally friendly adhesives from renewable materials (Huang and Li 2008; Li *et al.* 2009b; Liu and Li 2007; Wang *et al.* 2009; Wang *et al.* 2008b). Many attempts have been made to identify adhesives with good bonding strength, comparative water resistance, reasonable working life, and without formalde-hyde (Li *et al.* 2009a; Li *et al.* 2009b; Schwarzkopf *et al.* 2009; Wang *et al.* 2008a). Because soy protein is abundant, inexpensive, renewable, and easy to handle, soy-protein-based adhesives are believed to be some of the best alternative and potential adhesives to partly or completely replace the urea formaldehyde (UF) resin used in the

wood industry at present (Kumar *et al*. 2008; Mo *et al*. 2004). However, the low water resistance and bonding strength of soy protein-based adhesives still limit their extensive application, so they need to be modified to obtain better mechanical properties before being used in the wood industry.

The current focus on soy protein modification is expected to change its conformation into a random close structure (Zhang *et al*. 2007). During modification, soy protein changes its conformation from a folded structure to a random unfolded one, which always increases the interaction between soy protein-based adhesives and the substrate. Modifiers such as alkali (Cheng *et al*. 2004; Wang *et al*. 2008a), urea (Zhang and Hua 2007), sodium dodecyl sulfate (Li *et al.* 2009b; Mo *et al.* 2004; Zhong *et al.* 2003), and guanidine hydrochloride (Zhong *et al.* 2003) have been applied to the modifications of soy protein adhesive. With these methods, the bonding strength of soy protein adhesive increases, but the viscosity of the adhesive simultaneously increases significantly. To ensure lower viscosity of the adhesive, the soy protein concentration should be less than 15% (Li *et al.* 2009b; Mo *et al.* 2004; Wang *et al.* 2009; Zhang and Hua 2007), which results in lower production efficiency and higher energy and equipment consumption and prevents its wide application in the wood industry.

High viscosity adhesives are not accepted in the wood composites industry. Gao and co-authors (Gao *et al.* 2011, 2012a,b) have used polyethylene glycol (PEG) as a lubricant to reduce the apparent viscosity. Polyethyleneglycol diacrylate (PEGDA) is a kind of new structure polyfunctional methacrylate which has been widely used in the area of radiation cured coatings, superabsorbent polymers, adhesives, and pour point reducers. The PEGDA has a diene bond, which is expected to react with surface active group of soy protein. Therefore, in this study, PEGDA was introduced into the soybean meal (SM) adhesive system and used as a viscosity reducing agent and also as a crosslinking agent. The effects of PEGDA amount on the viscosity, gel content, water absorption of cured SM adhesives, and the water resistance of SM adhesives were investigated. Fourier transform infrared spectroscopy (FTIR) and solid-state ^{13}C NMR analysis were used to evaluate the cross-linked structure of these adhesives.

EXPERIMENTAL

Materials and General Methods

Poplar veneers with dimensions of $400 \times 400 \times 1.6$ mm (width$\times$ length$\times$ thickness) were obtained from Wen'an County of Hebei province, China, with a moisture content of 8.0%. SM, with an average protein content of 45.2% and moisture content of 5.0%, was purchased from Sanhe Hopefull Group Oil Grain Food Co. Ltd. It was milled into powder with an airflow crusher before use. Polyvinyl alcohol solution was prepared according to a method mentioned in previous literature (Qiu *et al*. 2012). PEGDA (200), provided by Sigma Chemical Co., had a molecular weight of 308 and viscosity of 0.12 Pa·s at 20 ± 2 ℃. All other chemicals used were analytical grade reagents from Beijing Chemical Reagents Co.

Preparation of SM Adhesives

SM adhesives were prepared according to the following procedures. Firstly, the SM (25 g) was suspended in polyvinyl alcohol solution (75 g), stirred to form a homogeneous system, and adjusted to a pH value of 9 to 9.5 using sodium hydroxide. Secondly,

PEGDA and ammonium persulfate (2% based on the PEGDA amount, used as an initiator) were added to the above solution and mixed uniformly. Finally, the resulting homogeneous mixture was stored at ambient temperature before use and had a solids content of about 29%.

Rheological Properties of Adhesives

Rheological measurements of the modified SM adhesives were performed using a rheometer (Brookfield R/S+CPS, American) with a parallel plate fixture (20 mm diameter). The distance was set to 1 mm for all measurements. Experiments were conducted under steady shear flow at 23 ^{o}C. Shear rates ranged from 10 to 240 s^{-1} at 10 s^{-1} increments. All measurements were conducted in duplicate, and the average value was reported.

Gel Content and Water Absorption of Curing Adhesives

The cured adhesive samples were immersed in water at 63 ^{o}C for 3 h to evaluate the water resistance of the adhesives. The gel content and water absorption values of cured adhesives were calculated using the following equations,

$$\text{Gel content} = \frac{m_d}{m_t} \times 100\%$$ (1)

$$\text{Water absorption} = \frac{m_w}{m_d} \times 100\%$$ (2)

where m_t, m_w, and m_d are the weight of the sample before immersion, the water uptake weight, and the dried weight after swelling, respectively.

Preparation of Plywood Samples

Three-layer poplar plywood (400 × 400 × 4.5 mm) was molded using a laboratory hot press under the following conditions: an adhesive spread rate of 150 to 180 g/m^2, a hot press temperature of 150 ^{o}C, a hot press pressure of 1.0 MPa, and 300 s of hot press time. After hot pressing, the prepared plywood was stored at 23 ^{o}C and 50% relative humidity for at least 24 h before testing the wet shear strength.

Wet Shear Strength Measurement

The wet shear strength of the plywood was determined in accordance with the procedure described in the China National Standard GB/T 9846.3-2004 (Standardization Administration of The People's Republic of China 2004) for Type II plywood. Plywood prepared as mentioned above was cut into shear specimens, submersed in water at 63 ^{o}C for 3 h, and then dried at room temperature for 10 min before the shear strength testing. The force (N) that damaged the bonded wood specimen was determined by a tensile machine at a speed of 10.0 mm/min. Wet shear strength (MPa) was calculated using the following equation, and all adhesive strength data reported are average values of eight replication tests.

$$\text{Wet shear strength (MPa)} = \frac{\text{Force } (N)}{\text{Gluing area } (m^2)}$$ (3)

Fourier Transform Infrared (FTIR) Spectroscopy of SM Adhesives

On the basis of the shear adhesion results, the SM adhesive and modified SM adhesive (4% PEGDA added) were selected for further characterization. The adhesives were freeze-dried at -70 $^\circ$C for 24 h and used as uncured adhesives, and the cured adhesive samples were prepared by placing the SM adhesive and modified SM adhesive (4% PEGDA added) in an oven at 150 $^\circ$C until a constant weight was reached. All samples were then ground into powder.

The FTIR spectra of uncured and cured adhesives were recorded on a Nicolet 380 spectrometer (Nicolet Instrument Corporation, Madison, WI) over the range of 400 to 4000 cm^{-1} with a 4 cm^{-1} resolution and 32 scans.

^{13}C CP-MAS NMR spectra

The PEGDA, SM adhesive, and modified adhesives samples were hardened at 150 $^\circ$C for 3 h in an oven. Being ground finely for solid-state ^{13}C NMR analysis, the prepared samples were analyzed by solid-state cross polarization/magic angle spinning (CP/MAS). ^{13}C NMR spectra of samples were obtained at 100 MHz using a Bruker AV-III 400M spectrometer (Germany). Samples were packed in 4 mm zirconia (ZrO_2) rotors, and the measurement was performed using a CP pulse program with 1 ms match time and a 2 s delay between transients. Spinning rate was 5 kHz. Chemical shifts observed were expressed in parts per million (ppm).

RESULTS AND DISCUSSION

Effect of PEGDA on Rheological Properties of SM Adhesive

Viscosity is an important physical property that governs the adhesive behaviors of wood adhesives. High-viscosity adhesives are not suitable for use in the wood composite industry, while low-viscosity ones allow easy handling and good flowability on the wood surface (Qi and Sun 2011). The apparent viscosity and flow behavior curves of SM adhesives modified with different amounts of added PEGDA are shown in Figs. 1 and 2. It can be seen from the figures that the apparent viscosity of the adhesives obviously decreased as the added PEGDA amount increased; the apparent viscosity of the SM adhesives modified with 8% added PEGDA was reduced extensively, by about 35% compared with the control (2.43 Pa·s and 3.7 Pa·s at the lowest shear rate, respectively). The reason for this is that with the addition of PEGDA, a shielding between the protein molecules may be formed, which weakens the interaction between protein molecules, resulting in reduced viscosity of modified SM adhesives. Moreover, because the PEGDA is manufactured through esterification using methacrylic acid and polyethyleneglycol, and the latter can be used as a lubricating agent for soy protein, the introduced low-viscosity polyethylene-glycol segments can reduce the intermolecular forces and make the soy protein become homodisperse (Gao *et al.* 2012), which reduces the apparent viscosity of modified adhesives. Therefore, the modified SM adhesives have better flowability than the control.
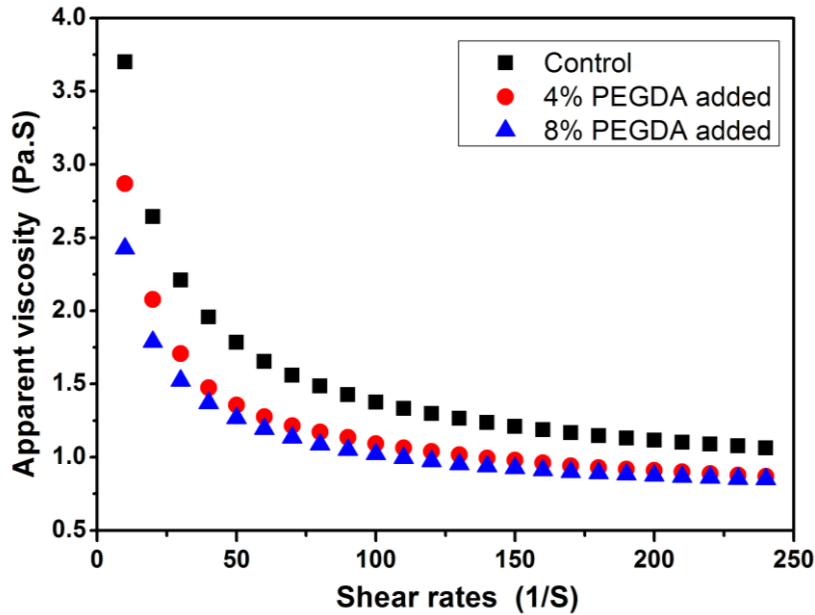
Fig. 1. Apparent viscosity dependence on the shear rate of SM adhesive

The apparent viscosity of all the SM adhesives and modified SM adhesives reduced as the shear rate increased, exhibiting shear thinning behavior, which can be expressed by the Herschel-Bulkley model (Wang *et al.* 2007),

$$\tau = \tau_o + K\gamma^n \tag{4}$$

where τ, τ_o, γ, n, and K are the shear stress (N/m^2), yield stress (N/m^2), shear rate (s^{-1}), flow behavior index, and consistency index, respectively. The τ_0, n, and K values were calculated using the least squares method to fit the equation by Origin 8.0 and are summarized in Table 1. The red lines in Fig. 2 are fitting curves.
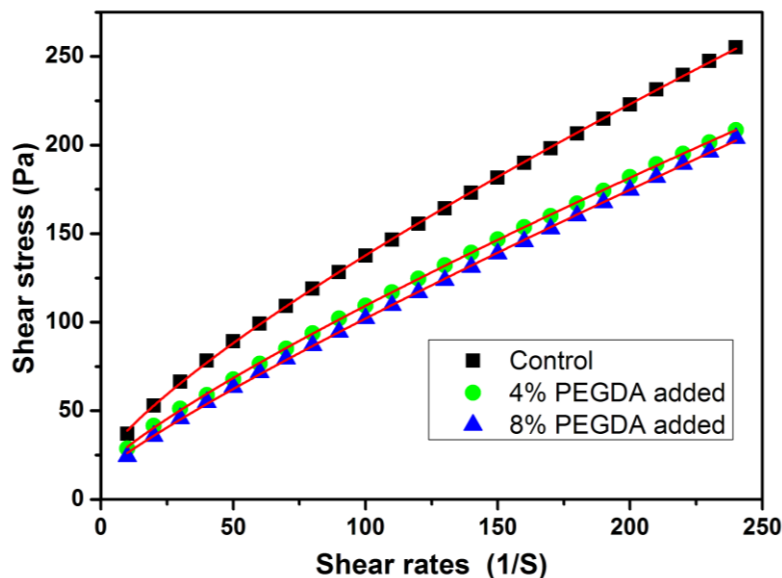

Fig. 2. Shear stress dependence on shear rate of SM adhesive

The *n* in the model is the measurement of non-Newtonian fluid degree; the farther *n* is from 1, the more obvious the non-Newtonian behavior (Tan *et al*. 2006). When *n* < 1, the apparent viscosity decreased as the shear rate increased, which is indicative of a pseudoplastic fluid with shear-thinning characteristics; if *n* > 1, the apparent viscosity increased as the shear rate increased, meaning dilatant plastic fluid shear with thickening properties. From Table 1, it can be seen that all of the SM adhesives were non-Newtonian pseudoplastic fluids with the property of shear-thinning. The reason the apparent viscosity decreased is that the degree of network structure damage of the SM adhesives, along with the shear rate, increased, and the further destruction of the structure leads to the apparent viscosity decrease. The added amount of PEGDA made the *n* increase from 0.7824 to 0.8718, showing that the pseudoplasticity of the modified SM adhesives decreased and that the non-Newtonian behavior was not significant compared with the SM adhesive.

Table 1. Rheological Parameters of Modified SM Adhesives

PEGDA added amount (%)	Yield stress, τ_o (N/m^2)	Consistency index, K	Flow behavior index, n	R-Square
0	19.1968	3.2291	0.7824	0.9999
4	15.5409	2.1000	0.8248	0.9999
8	14.3685	1.5823	0.8718	0.9998

The yield stress, (τ_o), is usually used to estimate the work that overcomes the starting resistance during the initial process of fluid shearing. Table 1 shows that as the added amount of PEGDA increased, the yield stress decreased significantly; the yield stress of the adhesive with 4% PEGDA decreased to 15.54 N/m^2, and that of the adhesive with 8% PEGDA decreased to 14.37 N/m^2, compared with 19.20 N/m^2 for the control. The decrease in yield stress indicates that the protein molecules in the adhesives became dispersed under the action of PEGDA, which caused the resistance to decrease during the process of fluid shearing. From Table 1, it can be seen that the regression equation had a high fitting degree: all of the correlation coefficients' R-squared values were all over 99.9%.

Water Resistance and Wet Shear Strength of Adhesives

Figure 3 displays the results of the gel content and water absorption of cured modified SM adhesives. As shown in Fig. 3, the gel content of cured adhesives gradually increased first and then decreased when the amount of PEGDA increased, and the water absorption had the opposite trend. The water absorption of cured adhesives decreased from 360% to 136%, and the gel content of the cured adhesives increased from 70% to 78% with an increase in PEGDA content from 0 to 4%, which is because the crosslinking density of the adhesives increases significantly (Zhang *et al.* 2007). This was reasonable because more reactive groups were introduced into the system. The change in gel content indicated that the crosslinking density of the modified adhesives increased at first and then decreased. When the added amount of PEGDA was 4%, the biggest gel content and lowest water absorption can be acquired. If the added amount of PEGDA was more than

4%, the redundancy of hydrophilic PEGDA caused an increase in water absorption and a reduction in the wet shear strength.
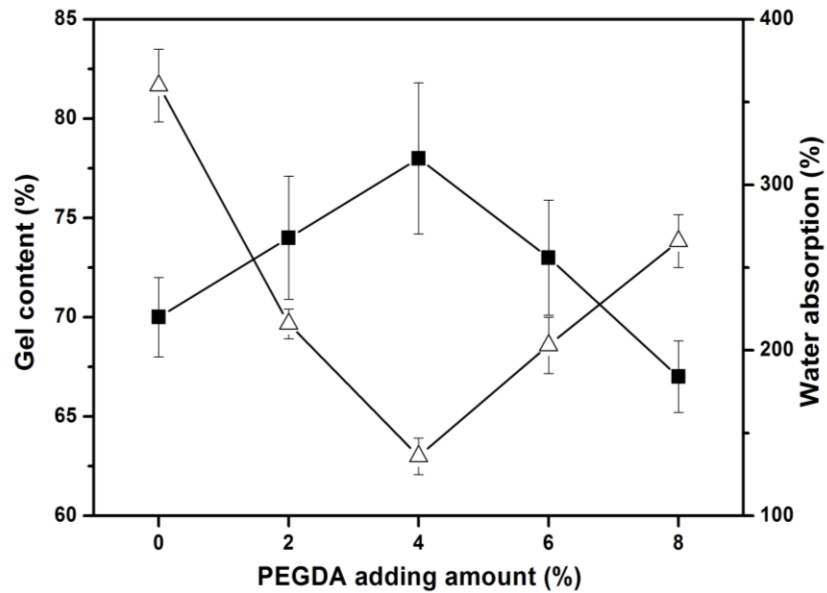

Fig. 3. Gel content and water absorption of cured modified SM adhesives. (■ Gel content; △ water absorption)

The wet shear strength of plywood bonded with modified SM adhesives is shown in Fig. 4. It can be seen that the wet shear strength of plywood bonded with modified SM adhesives increased when the PEGDA amount increased from 0% to 4%, and then decreased when the PEGDA amount further increased.
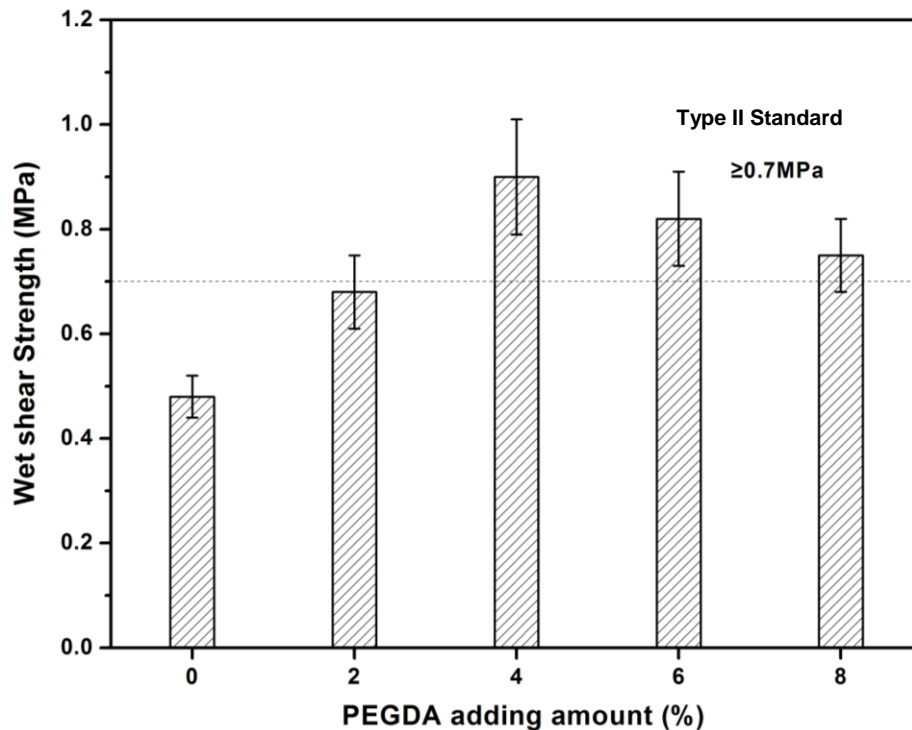

Fig. 4. The wet shear strength modified SM adhesives

Compared with the unmodified SM, the introduction of PEGDA did improve the water resistance of SM adhesives; the wet shear strength of the unmodified SM was only 0.48 MPa, but it was increased by 87.5% and reached 0.90 MPa with 4% PEGDA, which meets the interior plywood requirement ($\geq$ 0.7MPa, dashed line in Fig. 4) of the China National Standard (GB/T 9846.3-2004). Due to the formation of a crosslinking structure of cured PEGDA, the apparent viscosity decreased and the flowing ability increased as described above. The lower viscosity caused the distribution of adhesives to be more uniform during hot pressing and increased the spread area of wood and adhesives. The wet shear strength increased due to the fact that the glue attachments could be easily formed. The increased solid content could also have caused the increase in the wet shear strength. The result corresponded to the gel content and water absorption tests with modified SM adhesives.

Effect of PEGDA on the Structure of SM Adhesives

The FTIR spectra of different SM adhesive formulations are shown in Fig. 5. The broad band observed in the 3200 to 3500 cm^{-1} range corresponds to the stretching vibration of the free and bound N-H and -OH groups in all SM adhesives, which could form hydrogen bonding with the carbonyl group of the peptide linkage in the protein. The typical characteristic absorption bands of peptide linkage are related to C= O stretching at 1650.9 cm^{-1} (amide I), N-H bending at 1544.7 cm^{-1} (amide II), the absorption band at 1236.6 cm^{-1}, which is the contribution of C-N stretching, and N-H bending (amide III). Also, the absorption band at 1405.8 cm^{-1} resulted from C-N stretching (Zhang and Sun 2010; Fan *et al.* 2011). The new peaks of the modified SM adhesive with 4% PEGDA compared with no PEGDA occurred around the region of 812.1 cm^{-1}, 1636.6 cm^{-1}, and 1726.3 cm^{-1}, which are the C=C characteristic peak and C=O stretching vibration peak of PEGDA.
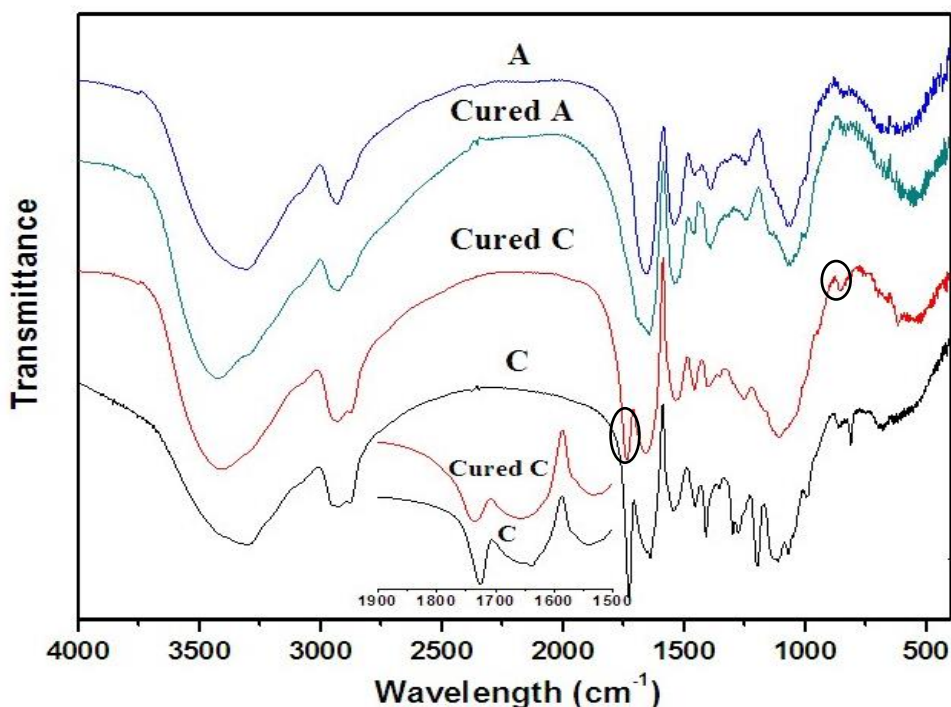

Fig. 5. FTIR spectrum of different SM adhesives (A: 0 PEGDA added; C: 4 % PEGDA added)

The C=C characteristic peak (1636.6 cm^{-1}) disappeared in cured PEGDA-modified SM adhesive (small figure in Fig. 5), which demonstrates that the crosslinking reaction of the PEGDA occurred successfully in the curing process of PEGDA-modified SM adhesive. And no other new absorption and vibration peaks were found or disappeared.
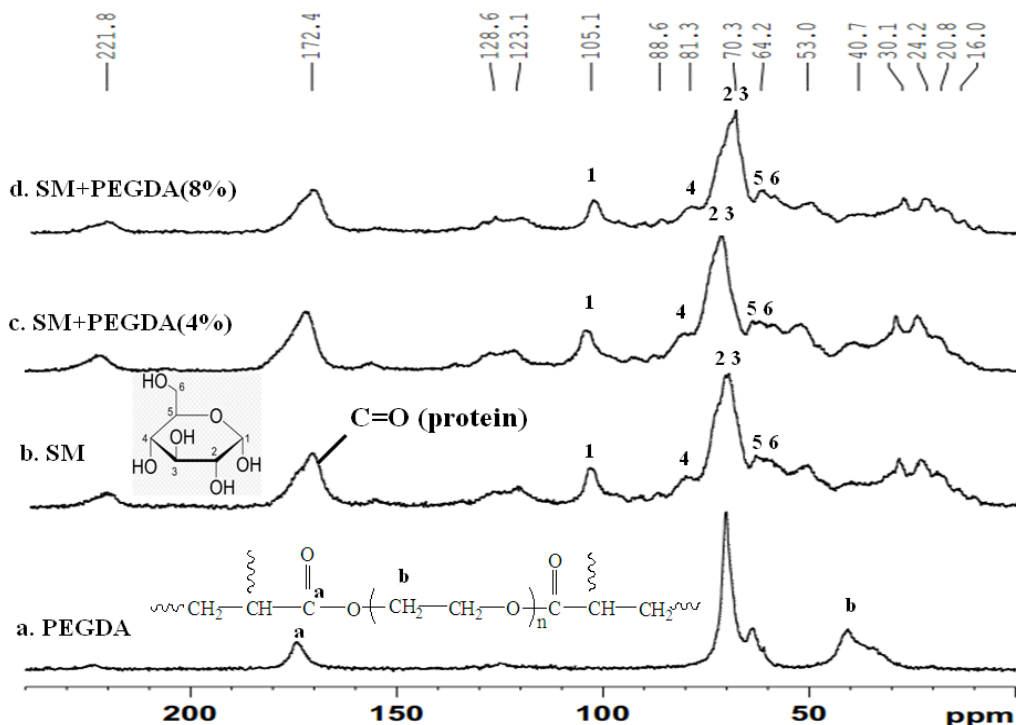

Fig. 6. Comparative solid-state ^{13}C NMR spectra of cured PEGDA, SM adhesive, and PEGDA+SM adhesives

Figure 6 shows the representative ^{13}C NMR spectrum of cured PEGDA, SM adhesive, and PEGDA-modified SM adhesives. The assignments of the different peak shifts were obtained from relevant literature (Amaral-Labat, *et al*. 2008; Moubarik *et al*. 2013). This measurement was used to show the reaction between soy meal adhesive and PEGDA.

Similar to the FTIR spectrum, C=C bond of PEGDA (125 ppm) disappeared due to the crosslinking reaction of PEGDA. The result of ^{13}C NMR spectroscopy also revealed that the spectrum of SM adhesive with different amounts were very similar to that of cured PEGDA and in particular the SM adhesive. The fact that no additional new groups were found in the ^{13}C NMR spectrum suggests that no reaction between the PEGDA and SM adhesive appears to have occurred.

Based on the spectrum of FTIR and ^{13}C NMR, it is not expected that the cross-linking reaction took place between the PEGDA and SM adhesives, so we inferred that interpenetrating polymer networks (IPNs) might be formed between cured PEGDA and SM adhesive systems, and the formed IPNs (as is shown in Fig.7) could be the reason that increased the wet shear strength (Son *et al*. 2005; Yoon *et al*. 2005). In the future, further research will be given to explain the formed IPNs in detail.

Fig. 7. Interpenetrating polymer networks (IPNs) of cured PEGDA and SM adhesive

CONCLUSIONS

1. All of the adhesives evaluated were non-Newtonian pseudoplastic fluids with the property of shear-thinning; the viscosity of modified SM adhesives effectively decreased by 35% compared with the addition of PEGDA.

2. When the amount of PEGDA was 4%, the gel content was highest and the water absorption was lowest.

3. The wet shear strength of the plywood panels bonded with PEGDA-modified SM adhesive was significantly improved from 0.48 MPa to 0.90 MPa when the amount of PEGDA was 4%.

4. The crosslinking reaction of the PEGDA occurred successfully during the curing process of PEGDA-modified SM adhesive; FTIR and ^{13}C NMR spectrum suggest that no reaction between the PEGDA and SM adhesive appears to have occurred.

5. Interpenetrating polymer networks (IPNs) might be formed between the cured PEGDA and SM adhesive system.

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