

Effects of polyisocyanate on properties and pot life of epoxy resin cross-linked soybean meal-based bioadhesive

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ABSTRACT: In this study, polyisocyanate (pMDI) was introduced into epoxy resin modified soybean meal-based bioadhesive to address the issue of low dry bond strength. Specifically, we investigated the effects of adding pMDI in terms of amount and storage time on dry bond strength, water resistance, and pot life of adhesive. Factors examined included shear strength, apparent viscosity, chemical reaction, crystallinity, and morphology of modified adhesives. Results indicated that the dry bond strength and water resistance of the resultant plywood was respectively improved 29.5% and 39.7% by adding 2% pMDI. In addition, the pot life of modified adhesive reached in 4 h. Results also shown that the cross-linking reactions between epoxy group and carbonyl as well as isocyano and amino increased the cross-linking density and formed a denser cross-linking network structure of cured adhesive. The composite cross-linked soybean meal-based adhesive is environmental-friendly and high-performance, which will promote the industrial application of the soy protein-based adhesives. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43362.

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INTRODUCTION

Formaldehyde-based adhesives, such as urea-, melamine-, phenol-formaldehyde resin, and their derivatives, constitute the majority of wood adhesives.¹ However, formaldehyde emissions and over-dependent nonrenewable petroleum resources of these synthetic resins have boosted a demand for the development of wood adhesives from renewable resources.

Soy-based adhesives are environmental-friendly protein adhesives, and are considered as desirable alternatives to formaldehyde-based adhesives.² However, their drawbacks include low bond strength and poor water resistance. Many chemical methods have been applied to address these issues, such as protein denaturing agent modification,^{3,4} soy protein molecule modification,^{5,6} and cross-linker modification.^{7,8} One effective method adopted by researchers in recent years was the composite modification through blending soy products with reactive resins. These reactive resins can react with functional groups of soy protein such as -OH, -COOH, and -NH₂ to form a cross-linked network, improving the bond strength and water resistance of the bonded panels. Qi and Sun⁹ blended synthetic latex with modified soy protein to fabricate plywood and found that improved water resistance even more than that of commercial urea-formaldehyde resin. In our previous studies, we used melamine-urea-formaldehyde resin¹⁰ and polyacrylic acid solution¹¹ to prepare soybean meal-based wood adhesives, which

shown excellent enhanced effectiveness. Other resins such as phenol-formaldehyde resin,¹² polyamide-epichlorohydrin,¹³ and Kymene¹⁴ have also been used to modify soy-based adhesive.

Composite modification is greatly dependent on the type of reactive resins used. Epoxies are effective modifier for the soy-based adhesives. A polyamide-epichlorohydrin (PAE)/soy flour adhesive system was developed and relative technology have achieved commercial application.¹⁴ Jang *et al.*¹⁵ used the reaction product of epichlorohydrin and ammonium hydroxide to cross-link soy flour-based adhesive for preparing interior plywood. Lei *et al.*¹⁶ adopted epoxy resin and melamine-formaldehyde resin as hybrid cross-linker to develop soy-based wood adhesives for type II and even type I plywood. However, our preliminary experiment found that epoxy resin modified soy-based adhesives have an issue of low dry strength. This may be related to the less mechanical interlocking between wood and the adhesive caused by macromolecular structure of soy protein. Dry strength is a very important property of plywood, which determined its processing performance. For example, an insufficient dry strength can cause seed breakage when mortising and cutting, which was unacceptable in the engineer flooring and furniture manufacturing industry.

Polyisocyanate (pMDI) is a versatile compound in the polyurethane industry, and has become an important wood binder to

produce the structural wood composite materials, such as oriented strandboard, exterior-grade particleboard and medium density fiberboard.^{17,18} Isocyanate is a highly reactive group and can react with compounds that possess “active” hydrogens, e.g., carboxylic acids, amides, and water. Gao *et al.*¹⁹ found that pMDI increased the bond strength of whey protein adhesive and formed strong chemical bonds in wood bond-line. Zhong and Sun²⁰ added methylene diphenyl diisocyanate in soy protein isolate/polycaprolactone blend to improve compatibility and obtain increased mechanical properties and water resistance. However, the limited pot life caused by the foaming of adhesive pose a problem. Gao *et al.*¹⁹ added 15 wt % of pMDI (liquid basis) into whey protein solution as cross-linker, obtaining a higher dry strength and better bond durability than that without pMDI. However, the pot life of blended adhesive was very short at about 30 min, which was unacceptable for commercial application. The severely shortened pot life caused by the high sensitivity of pMDI to water. During the reaction of pMDI and water, carbon dioxide were produced and resulted in the increase of adhesive volume and viscosity, leading to a low flowability and poor distribution, especially under high temperature condition in summer.

This study aimed to develop a soybean meal-based wood adhesive with excellent mechanical property and acceptable pot life by introducing epoxy resin and pMDI. Effects of pMDI addition amount and storage time on the properties of bonded plywood and the pot lives of blending adhesives were investigated. A rheometer was used to detect the change in apparent viscosity of blended adhesives. Fourier transform infrared (FT-IR) spectroscopy was used to examine the cross-linking reaction between the cross-linker and the soy protein molecules. The crystallinity and the morphological properties of the cured adhesives were respectively characterized with X-ray diffraction (XRD) and scanning electron microscope (SEM) to explore the enhancement mechanism.

EXPERIMENTAL

Materials

Soybean meal (43 wt % protein content) was supplied by Xiangchi Grain and Oil Co. Ltd. (Shandong, China). Commercial bisphenol-A epoxy resin with epoxide value (eq/100 g) of 0.41 to 0.47 and softening point of 12 to 20°C was purchased from Keyuan Fine Chemical Co. Ltd. (Weifang, China). Polyisocyanate with NCO content of 30 to 32% and viscosity of 150 to 250 MPa s (25°C) was produced by Chemical Industry Co. Ltd. (Taiyuan, China). Other chemical reactants were reagent grade and obtained from Chemical Reagents Co. Ltd. (Beijing, China). Poplar veneers with moisture content of 8.0% and dimensions of 400 mm × 400 mm × 1.5 mm were provided by a local plywood plant.

Adhesive Preparation and Apparent Viscosity Measurement

Soybean meal (SM) adhesive was prepared by adding soybean meal (28 g) into water (72 g) and stirred for 30 min at room temperature to form a homogeneous system. Epoxy resin (8% based on weight of SM adhesive) was added into the SM adhesive and stirred for 10 min to develop the epoxy resin (EP) modified soybean meal (SM/EP) adhesive. Different amounts of pMDI (1%, 2%, 3%, 4%, 5%, 6% based on weight of SM adhesive) were

incorporated into the SM/EP adhesive and stirred for 5 min to prepare the pMDI modified SM/EP (SM/EP/pMDI) adhesives.

Apparent viscosity of adhesive was determined by a rheometer (Brookfield R/S + CPS, American) with a parallel plate fixture (20 mm diameter). The distance between cone and plate was set to 1 mm, and the shear rate ranged from 10 to 240 s⁻¹ at 10 s⁻¹ increment. The measurements were conducted in duplicate under a steady shear flow at 23°C and the average value was reported.

Plywood Preparation and Evaluation

Three-ply poplar plywood were prepared in this study. The adhesives were coated on both sides of the core veneer using a brush. The glue spreading was 360 g/m². The adhesive-coated veneer was stacked between two uncoated veneers with the grain direction of the two adjacent veneers perpendicular to each other. The stacked veneers were hot-pressed at 1.0 MPa and 120°C for 6 min. Two plywood were made for each adhesive.

The shear strength of plywood was determined according to the procedure described in China National Standard for Type II plywood (GB/T 9846.3-2004). After equilibrated for at least 24 h under room condition, the bonded plywoods were cut into specimens with dimensions of 100 mm × 25 mm (gluing area of 25 mm × 25 mm). The dry shear strength were determined using a common tensile machine operating at a speed of 10.0 mm/min. The force required to break the glued specimen was recorded. The shear strength was calculated as the ratio of the force/glue area. The reported strength data were averaged over six specimens. Meanwhile, the cut specimens were immersed in water at 63 ± 3°C for 3 h, removed from water, and cooled at room temperature for 10 min before the wet shear strength measurements under the same testing condition. Wood failure of samples after shear strength testing were determined based on the area method. The glue interface was broken after shear strength testing. A part of wood tissue was teared from one veneer and bonded on another veneer. The ratio of the teared area/glue area represents the wood failure.

FT-IR, XRD, and SEM Measurement

The adhesives were placed in an oven at 120 ± 2°C to cure completely, and then ground into fine powder. The powder were mixed with KBr crystals at a mass ratio of 1/100, and pressed in a special mold to form a sample folium. The FT-IR spectra were recorded using a Thermo Nicolet 6700 FT-IR (USA) over the range of 400 to 4000 cm⁻¹ with a 4 cm⁻¹ resolution and 32 scans.

X-ray diffraction (XRD) patterns were recorded on a XRD diffractometer (D8 ADVANCE, BRUKER, German) using a cobalt source and 0.2 theta scan ranging from 5° to 60° at 45 kV and 30 mA. Crystallinity were calculated by its included software, EVA. Each adhesive formulation was tested three times and the average value was reported.

The adhesives were cured in an oven at 120 ± 2°C. The cured adhesive films with a thickness of about 1.5 mm were fractured, and the fractured cross-sections were examined using a Hitachi S-3400N emission scanning electron microscope (Hitachi Scientific Instruments, Tokyo, Japan). Before examining, the fractured cross-sections were coated with 10 nm Au/Pd film using a

Table I. Dry Strength and Wood Failure of Plywood Bonded by the Soybean Meal-Based Adhesives

Adhesive	Dry strength (MPa)	Wood failure (%)
SM	1.15 ± 0.11	1–5
SM/EP	1.32 ± 0.12	5–10
SM/EP/1%pMDI	1.41 ± 0.16	10–20
SM/EP/2%pMDI	1.71 ± 0.15	70–80
SM/EP/3%pMDI	1.75 ± 0.18	80–90
SM/EP/4%pMDI	1.82 ± 0.13	100
SM/EP/5%pMDI	1.80 ± 0.11	100
SM/EP/6%pMDI	1.84 ± 0.15	100

Q150T S Turbo-Pumped Sputter Coater/Carbon Coater (Quorum Technologies Ltd., UK).

RESULTS AND DISCUSSION

Dry Strength and Water Resistance of Plywood

Native soy proteins are loose in structure and display high viscosity and low solid content when dissolved in water.²¹ In our study, the SM adhesive with native soy proteins exhibited a low dry strength (1.15 MPa), as shown in Table I. After the introduction of EP, the adhesive shown an increased dry strength (1.32 MPa). However, the low wood failure (5–10%) indicated insufficient bonding, which was adverse for subsequent panel processing. When 2% pMDI was added, the dry strength of plywood was further improved by 29.5% to 1.71 MPa. These significant improvements may be attributed to the cross-linking reaction between soy proteins and EP/pMDI. Because the bond strength of adhesive was higher than the breaking strength of poplar veneer, the specimens had a wood failure of 100%. Thus, the higher pMDI addition did not observably further increase the dry strength.

The wet shear strength of the adhesives are listed in Table II. Soy proteins possess many polar and apolar side groups. Most apolar groups are hidden in the interior of molecules, while polar parts are exposed outside.²² This gives the native soy protein adhesive water sensitivity and low wet shear strength (about 0.28 MPa). Our findings show that EP significantly improved the wet shear strength of bonded plywood. This may

be attributed to the cross-linking reaction between epoxy groups and varieties of functional groups in soy protein molecules. Wet shear strength of plywood were further enhanced by the introduction of pMDI. At the start of blending, wet shear strength increased as the added pMDI increased. It was improved by 39.7% compared with EP cross-linked adhesive and reached a maximum value of 1.34 MPa in SM/EP/6%pMDI adhesive. After 2 h, 5% and 6% pMDI modified SM/EP adhesives showed an obvious reduction in the wet shear strength. This indicated that the adhesives were foamed and exerted an adverse impact on bonding. After 4 h, a similar decrease was appeared in 3% and 4% pMDI modified SM/EP adhesives. The pot life of adhesive can be determined as the time after blending modifier with adhesive when the adhesive no longer gives the required bond strength.²³ Therefore, results suggested that only the SM/EP/2%pMDI adhesive can reach an acceptable pot life of 4 h, which met the requirement of commercial application.

Effects of pMDI Modification on the Pot Life of Adhesive

The pot life of an adhesive can be also determined as the time after blending the modifier with the adhesive, when the viscosity of the adhesive is too high for normal use. Viscosity is an important physical parameter that largely affects adhesive behavior of adhesive. Correct viscosity gives adhesive good flowability and allows easy handling to obtain high bond strength of bonded product.²¹ We selected the apparent viscosity of adhesive at a shear rate of 10 s⁻¹ to investigate foaming caused by adding pMDI and evaluate the pot life of modified adhesive, as shown in Table III. At the start of blending, the SM adhesive had the highest apparent viscosity because of the finitely unfolded soy protein molecules. After EP was introduced, the apparent viscosity distinctly decreased and retained the lowest value during the storage process. Moreover, the apparent viscosity increased with the increased pMDI and the extended storage time. In general, the viscosity of 5000 to 25,000 mPa s is a suitable range for adhesive that is used to bond plywood.²⁴ As shown in Table III, the apparent viscosity of SM/EP/4%pMDI for a storage time of 2 h and that SM/EP/3%pMDI of 4 h were over the upper limit. The SM/EP/2%pMDI adhesive showed an acceptable apparent viscosity within 4 h. It was suggested that the pot life of adhesive modified by over 3% pMDI was less than 4 h and that modified by 2% pMDI can reach 4 h.

Table II. Wet Shear Strength of Plywood Bonded by the Soybean Meal-Based Adhesives with Different pMDI Content and Storage Time

Adhesive	Wet shear strength (MPa)				
	0 h	2 h	4 h	8 h	12 h
SM	0.28 ± 0.17	0.30 ± 0.19	0.29 ± 0.16	0.28 ± 0.13	0.27 ± 0.15
SM/EP	0.78 ± 0.11	0.76 ± 0.10	0.75 ± 0.11	0.74 ± 0.12	0.71 ± 0.14
SM/EP/1%pMDI	0.98 ± 0.13	0.96 ± 0.14	0.88 ± 0.12	0.74 ± 0.15	0.72 ± 0.14
SM/EP/2%pMDI	1.09 ± 0.12	1.08 ± 0.11	0.93 ± 0.10	0.84 ± 0.13	0.73 ± 0.12
SM/EP/3%pMDI	1.12 ± 0.11	1.09 ± 0.12	0.78 ± 0.11	0.74 ± 0.11	0.72 ± 0.10
SM/EP/4%pMDI	1.15 ± 0.10	1.11 ± 0.11	0.75 ± 0.11	0.74 ± 0.13	0.64 ± 0.13
SM/EP/5%pMDI	1.22 ± 0.15	0.72 ± 0.14	0.69 ± 0.16	0.59 ± 0.17	0.56 ± 0.15
SM/EP/6%pMDI	1.34 ± 0.15	0.65 ± 0.18	0.61 ± 0.17	0.55 ± 0.17	0.47 ± 0.16

Table III. Apparent Viscosity of the Soybean Meal-Based Adhesives at the Shear Rate of 10 s^{-1}

Adhesive	Viscosity (mPa s)				
	0 h	2 h	4 h	8 h	12 h
SM	22,550	24,350	24,810	25,270	34,450
SM/EP	5127	6014	6790	10,990	17,850
SM/EP/2%pMDI	12,420	23,370	25,730	29,820	49,350
SM/EP/3%pMDI	12,970	19,730	30,750	48,500	85,450
SM/EP/4%pMDI	13,050	27,950	35,950	65,920	94,610
SM/EP/5%pMDI	14,082	41,290	71,090	107,300	284,900
SM/EP/6%pMDI	16,980	92,540	154,100	146,300	171,800

This accords with our results obtained in the bond strength evaluation.

To intuitively characterize the pot life, adhesives were placed in an oven with a temperature of 40°C , and their foaming degrees are shown in Figure 1. During the storage process, the SM adhesive appeared to swell slightly just like in flour fermentation for baking bread (as shown SM-0h and SM-8h). The SM/EP adhesive showed the least foaming degree and the best flowability, and was spread out on the glass plate (as shown SM/EP-0h and SM/EP-12h). The pMDI is a highly reactive polymer that can react with water and release carbon dioxide. The water of adhesive is gradually consumed as the reaction progresses, and then the viscosity is increased.

As shown in Figure 1, the foaming degree increased with more added pMDI and the extended storage time. When over 5% pMDI was added, obvious foaming behavior appeared in 2 h (as shown SM/EP/5%pMDI-2h and SM/EP/6%pMDI-2h). Meanwhile, serious foaming occurred within 4 h in over 3% pMDI modified SM/EP adhesive (as shown SM/EP/3%pMDI-4h and SM/EP/4%pMDI-4 h). These foaming soybean meal-based adhesives had high viscosity and low flowability, making it difficult to permeate in wood and form mechanical interlocking during hot pressing. This resulted in the low bond strength and water resistance of the prepared plywood. For the SM/EP/2%pMDI adhesive, it still had certain flowability, and the foaming degree was acceptable even storage for 4 h (as shown SM/

EP/2%pMDI-4h). The obtained pot lives of adhesives were in accordance with our findings in the bond strength and viscosity measurement.

Cross-Linking Mechanisms of pMDI Modified SM Adhesive

The FT-IR spectra of the cured soybean meal (SM) adhesive, epoxy resin modified SM (SM/EP) adhesive, and pMDI blended SM/EP (SM/EP/pMDI) adhesives are given in Figure 2. The broad band between 3200 and 3500 cm^{-1} corresponded to free and bound N-H and O-H groups, which are the functional groups forming hydrogen bond with wood.²⁵ The peak observed at 2930 cm^{-1} was attributed to C-H stretching vibrations of methyl groups. Three typical characteristic absorption bands of amide were observed at 1660 , 1539 , and 1234 cm^{-1} , which were assigned to C=O stretching (amide I), N-H bending (amide II), and N-H in plane and C-N stretching vibration (amide III), respectively. The absorption bands at 1396 cm^{-1} and 1050 cm^{-1} were respectively attributed to the stretching vibration of COO- and C-O of hydroxyl groups bonded to carbon atoms.

Comparing SM and SM/EP adhesive, we found that there were no free epoxy group existed in the SM/EP adhesive, suggesting all EP reacted with soy protein. The peak at 1396 cm^{-1} weakened significantly and a new absorption was observed at 1730 cm^{-1} , which should be attributed to the esterification between epoxy groups and carbonyl groups of soy protein.²⁶ By this reaction, the loose soy protein molecules were cross-linked

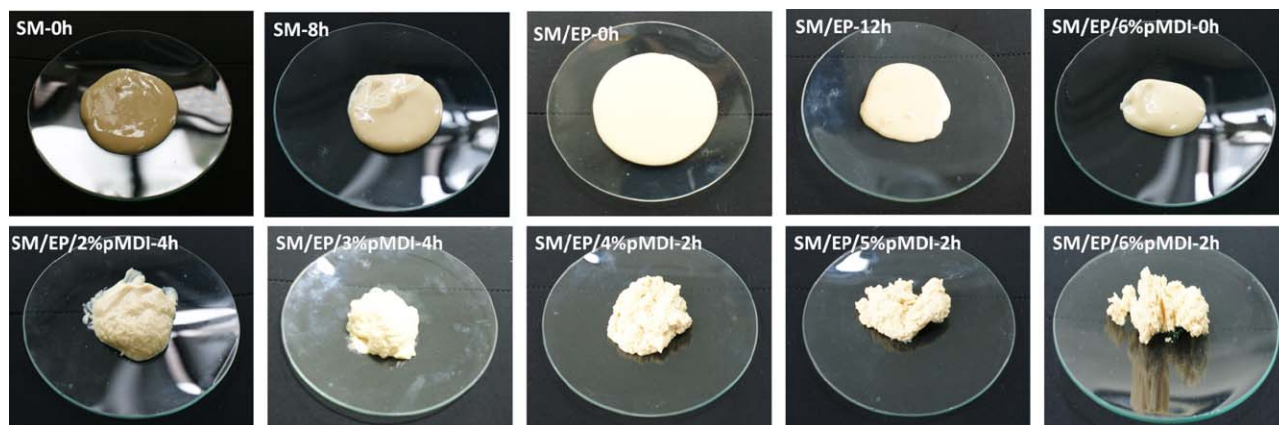


Figure 1. Foaming of the pMDI modified soybean meal-based adhesives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

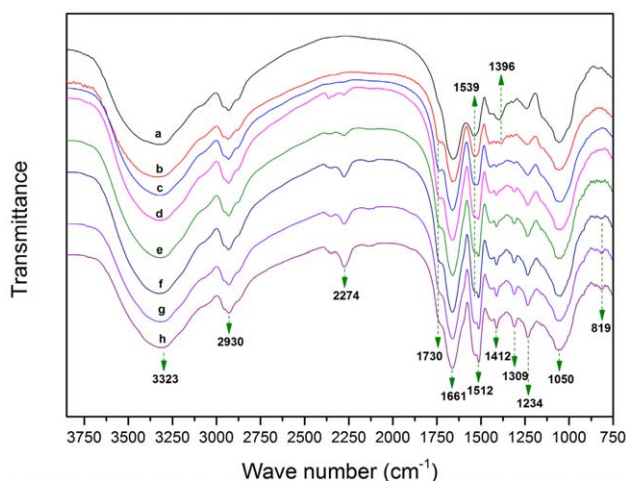


Figure 2. FT-IR spectra of the adhesives: a (SM adhesive), b (SM/EP adhesive), and c (SM/EP/1%pMDI adhesive), d (SM/EP/2%pMDI adhesive), e (SM/EP/3%pMDI adhesive), f (SM/EP/4%pMDI adhesive), g (SM/EP/5%pMDI adhesive), h (SM/EP/6%pMDI adhesive). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

together and formed dense cross-linking network structure which would improved the water resistance of adhesives. When of pMDI was introduced, the characteristic peak of isocyanate (NCO) was not observed in the spectrum of cured adhesive with a small level (1%) but existed in that with over 2% pMDI, and the signal intensity of the peak increased with the increasing pMDI addition. These residual NCO groups will react with hydroxyl groups of veneer during the hot pressing process,¹⁹ which may be the reason for the improvement of the dry bond strength. Moreover, the peak attributed to N–H bending (1539 cm^{-1}) of amide decreased and eventually disappeared after incorporating pMDI, which demonstrated the cross-linking reaction of NCO group and amino ($-\text{NH}_2$) in soy protein molecules. However, the produced urea linkage at 1640 cm^{-1} was obscured by amide I and was not observed in the spectra.¹⁹ When over 4% pMDI was added, the epoxy group (819 cm^{-1}) appeared and the peak at 1730 cm^{-1} decreased gradually, which indicated that a high level of pMDI adverse to the cross-linking of EP and carbonyl groups of soy protein.

The X-ray diffraction patterns of the SM adhesive and its hybrid adhesives are shown in Figure 3, and the calculated crystallinity was listed in Table IV. The SM adhesive showed two diffuse X-ray peaks at the 2θ angle about 9° and 20° , which belong to the α -helix and β -sheet structure of soy protein, respectively.²⁷ Compared with the SM and its modified adhesives, the peak at 2θ of 20° disappeared, which confirmed the cross-linking reaction between the EP and soy protein. In addition, the intensity of pattern was decreased obviously when EP was introduced, and further decreased after the introduction of pMDI to the

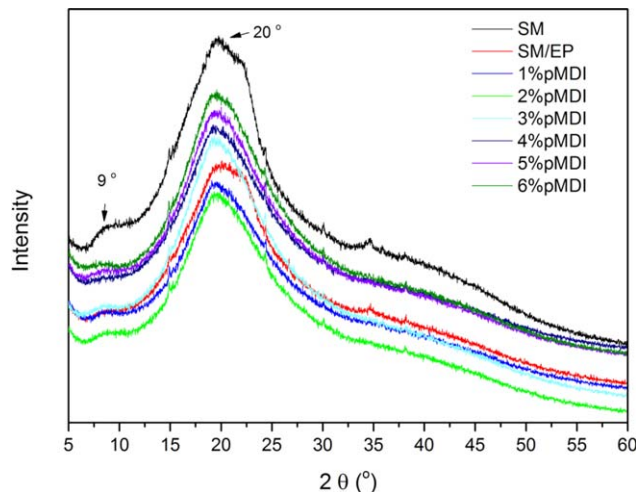


Figure 3. X-ray diffraction patterns of the cured SM adhesive, SM/EP adhesive, and SM/EP/pMDI adhesives with 1, 2, 3, 4, 5, and 6% pMDI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

minimum in the SM/EP/2%pMDI adhesive, then increased with the pMDI addition increased. Similarly, the crystallinity of cured adhesive also show the same variation trend. Generally, increasing cross-linking in an adhesive reduces its crystallinity.²⁸ The crystallinity decreased apparently from 14.1 to 11.2% after introducing EP, and it further decreased when pMDI was added to the minimum of 10.3% in the SM/EP/2%pMDI adhesive, indicating the continually increased cross-linking density of cured adhesive which enhanced the mechanical properties. This is in accordance with previous study.^{29,30} Continue increased the pMDI addition led to increased crystallinity, probably due to the increased intensity of cured adhesive system caused by the curing of residual pMDI, which indicated that the added pMDI was superfluous and caused the cost rising.

Scanning electron micrographs of the cross-sections of the cured SM, SM/EP, and SM/EP/pMDI adhesives with 1, 2, 3, 4, 5, and 6% pMDI are shown in Figure 4. A large number of cracks were observed on the cross-section of SM adhesive, and the entire cross-section was very loose. The flawed and loose cross-section resulted from water vaporization of adhesive in curing process, which was easily intruded by moisture and led to a low water resistance.¹¹ After EP was added, fewer cracks were formed and the cross-section became compact but some wrinkles, which resulted from the cross-linking reaction between EP and soy protein molecules. For the SM/EP/1%pMDI adhesive, the rough and loose cross-section structure was produced, which resulted from the pMDI foaming. With the introduction of 2% pMDI, cracks and wrinkles disappeared and a homogeneous cross-section was produced, which was attributed to the further cross-linked soy protein molecules with pMDI and the

Table IV. The Crystallinity of the Cured SM Adhesive, SM/EP Adhesive, and SM/EP/pMDI Adhesives with 1, 2, 3, 4, 5, and 6% pMDI

Adhesive	SM	SM/EP	1%pMDI	2%pMDI	3%pMDI	4%pMDI	5%pMDI	6%pMDI
Crystallinity (%)	14.1 ± 0.9	11.2 ± 0.1	10.4 ± 0.1	10.3 ± 0.1	10.8 ± 0.2	10.9 ± 0.2	11.8 ± 0.1	11.9 ± 0.1

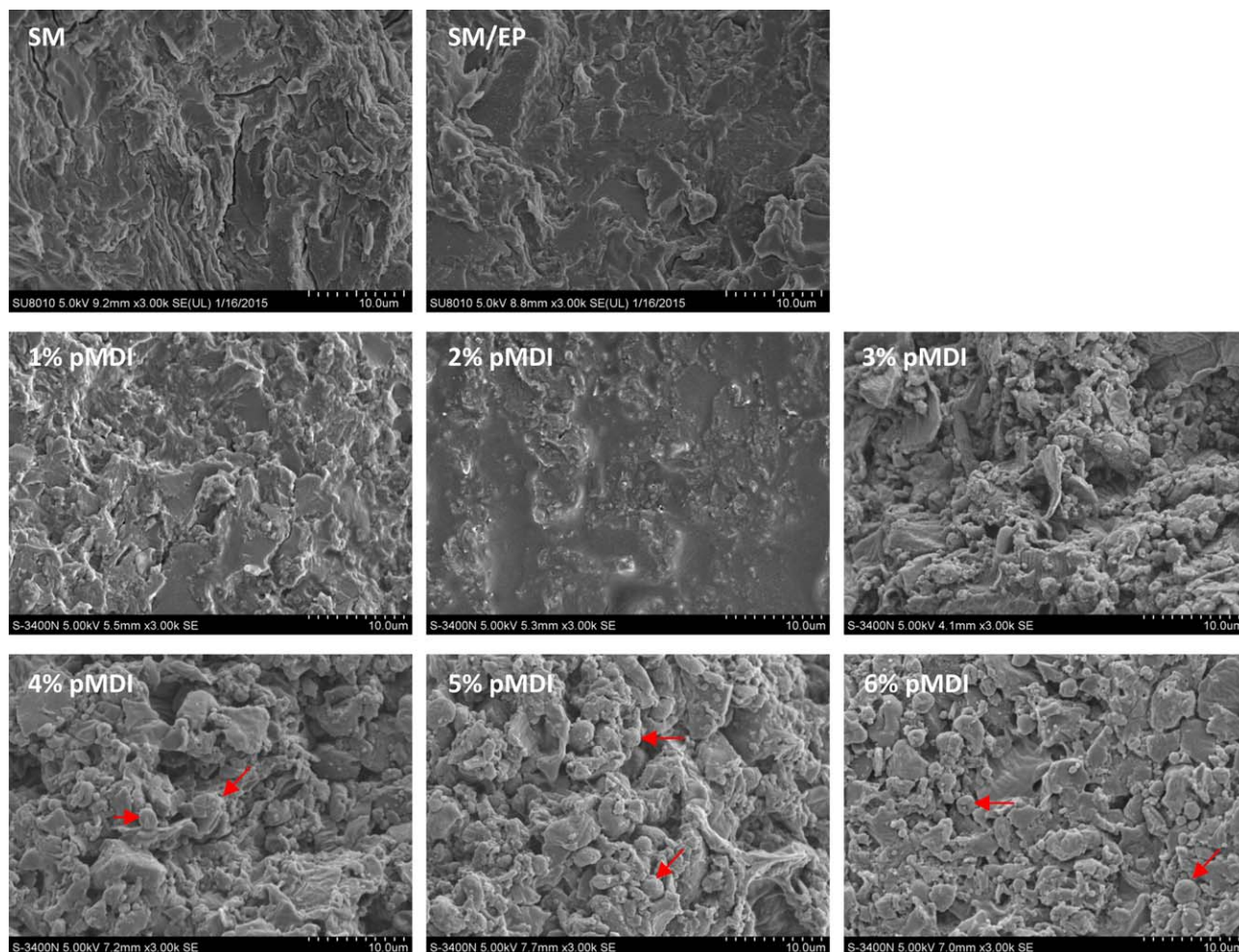


Figure 4. SEM image of the cured SM adhesive, SM/EP adhesive, and SM/EP/pMDI adhesives with 1, 2, 3, 4, 5, and 6% pMDI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

balance between cross-linking and foaming in adhesive system. With the further increased pMDI addition, the cross-section became more rough and loose and some small spherical particles (arrows) were formed, revealing the increased degree of foaming of adhesives, and worsening the mechanical properties and processability of bonded plywood. The schematic diagram

of the adhesive cross-linking network formation are shown in Figure 5. By the cross-linking reaction between EP/pMDI and soy protein molecules, the cross-linking density of cured adhesive system was increased and a denser cross-linking network structure was formed, improving the bond strength and water resistance of resultant plywood.

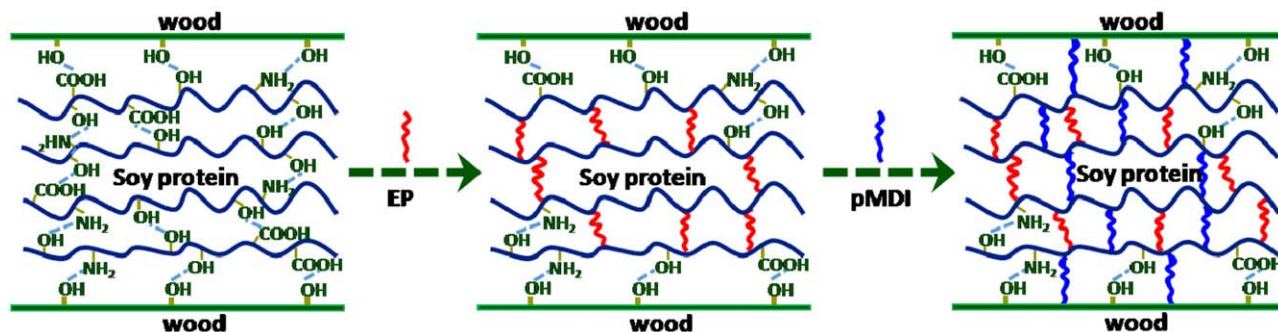


Figure 5. The cross-linking network of composite cross-linked soybean meal-based adhesive. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

This study demonstrated that EP is an active modifier for soybean meal-based adhesives. Through cross-linking reaction between epoxy groups and carbonyls in soy protein molecules, the cross-linking density of the cured adhesives increased, forming a denser cross-section, and improving the bond strength and water resistance of bonded plywood. In addition, pMDI further increased the bond strength and water resistance of plywood. The cross-linking density was further increased and formed a homogeneous cross-section of cured adhesives. The high reactivity of isocyanate groups promoted the reaction with amino of soy protein. This was the main reason for the considerable improvement of dry bond strength and water resistance. However, high amounts of pMDI addition are not suitable for soy protein adhesive modification. Due to high reactivity, the isocyanate group can react with the water of the system to foam in the adhesive. The viscosity of adhesive increased and thus does not meet the requirements of commercial application. Moreover, our findings show that the dry bond strength and water resistance of the resultant plywood was respectively improved 29.5% and 39.7% by adding 2% pMDI, and an acceptable pot life of 4 h is obtained. This study benefits the industrial application of the soy protein-based adhesive.

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