Article

Carboxymethylated Lignin Reinforcement of SPI Adhesive: Enhancing Strength, Antimicrobial, and Flame-Retardant Properties without Excessive Alkali Introduction

Changjiang Sun, Fengxiang Cao, Yecheng Xu, Jiao Feng, Keyan Wang, Zhen Fang,* and Yangbing Wen*

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ABSTRACT: To address the challenges associated with formaldehyde emissions in engineered wood adhesives and simultaneously enhance adhesive properties related to water resistance, fire resistance, and mold resistance, a novel environmentally sustainable biomass-based adhesive was formulated. In this work, kraft lignin was carboxymethylated and then blended with the soy protein isolate (SPI)-based adhesive, the dry and wet shear strength of the plywood bonded by the resultant adhesive was enhanced from 1.10 and 0.63 MPa to 1.73 and 1.23 MPa, respectively, resulting in improvements of 157% and 195%. Carboxymethylated lignin (CML) significantly improved the mold resistance and flame-resistance residual rate of the adhesive and decreased the water absorption rate from 190% to 108%.

Furthermore, the adhesive exhibits outstanding flame-retardancy, with self-extinguishing capability rendering it suitable for industrial production. In addition, we also evaluated the performances of resulting adhesives cured with different diepoxides and triepoxides, and the comparisons of the adhesive in this work to commercial urea glue and soy protein-based adhesives were conducted. To our delight, the SPI-10CML adhesive presented comparable or even improved performances, showing its promising practical applications such as for fire doors.
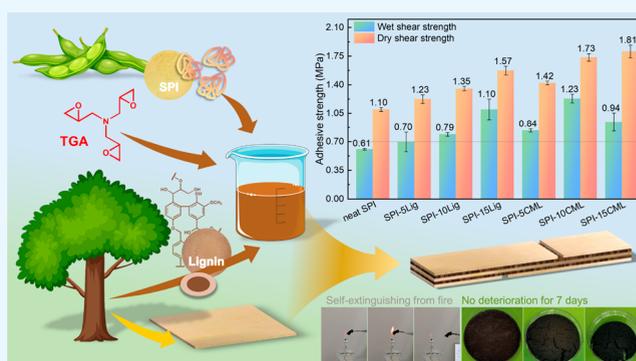
1. INTRODUCTION

Striving to break free from the constraints of petroleum resources and exploring new alternatives is a concerted effort among many scholars, particularly in the realm of artificial board adhesives.[1−3] Currently, petroleum-derived and aldehyde-based adhesives represent the mainstream choice for wood panel adhesives, which not only accelerate the fossil fuel crisis but also lead to the release of aldehydes into the environment, significantly impacting the health of users.[4−6] It is of great significance and importance to replace petroleum derivates with sustainable biobased materials.[7,8] Soy protein isolate (SPI), as a naturally renewable, low-pollution, and biodegradable biomass material, holds immense potential in the field of wood panel adhesives.[9,10]

SPI was known to possess a high content of hydrophilic groups that significantly affects the strength of adhesives, particularly in terms of wet strength.[7] Additionally, due to the rich nutritional composition of SPI, enhancing the antimicrobial properties of adhesives has become a significant research focus for scholars.[11−13] Many researchers lean toward premodifying SPI to improve the strength and antimicrobial properties of adhesives.[11,12] While these modifications to SPI yield favorable results, they undoubtedly increase industrial costs and reduce the competitiveness of the product in the

market. The prospects for industrial application of modified SPI are, therefore, very limited. One typical convenient and efficient approach is to introduce additives to the adhesive to enhance its performance.[13,14]

Adhesives based on proteins require further enhancement of wet strength and antibacterial properties.[15,16] Among natural polymers, lignin appears to be more adept at achieving these objectives.[17] Lignin, with its abundant aromatic rings, exhibits favorable structural properties.[18−20] Some researchers have even utilized lignin as a substrate to fabricate adhesives for engineered wood; however, aldehyde compounds were employed into the process.[1] In terms of antibacterial performance, lignin demonstrates unparalleled advantages over other natural polymers.[21] In recent years, there has been a proliferation of research using lignin as a substrate to develop medical antibacterial materials, showcasing lignin's extraordinary antibacterial capabilities.[22,23]
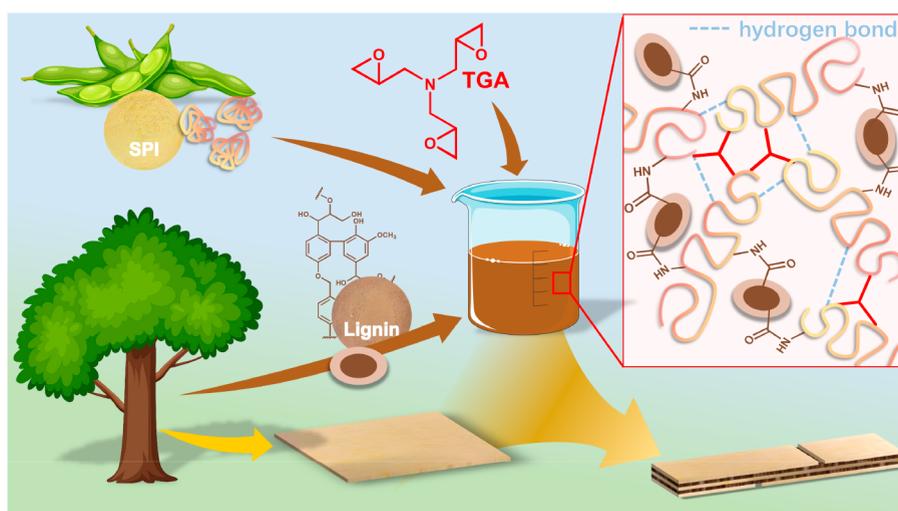
Figure 1. Schematic illustration of the preparation of CML-enhanced soy protein-based adhesive.

Moreover, lignin is abundantly available in nature, extracted during the pulping and papermaking processes. It serves as a widely utilized industrial resource due to its low cost, ensuring that the improvement of adhesive performance does not impose additional financial burdens. Actually, lignin has been widely introduced into soy protein-based adhesives and demonstrated outstanding capacity to improve the wet shear strength and antibacterial performance.[24,25] Lignin, however, possesses numerous disadvantages, such as exceptionally low solubility in neutral water. To dissolve more lignin, it is necessary to elevate the pH of the solution, albeit at the risk of inducing protein denaturation in SPI due to excessively high pH, significantly diminishing the bonding strength of the final adhesive product.

This study introduces an innovative approach to hydrophilic modification of lignin (Figure 1): carboxymethylation modification to enhance the solubility. Carboxymethylated lignin (CML) also acts as a stabilizer in the system, reducing viscosity and enhancing the workability of the adhesive.[26−28] This has a favorable effect on extending the shelf life of the adhesive. In this study, a novel SPI adhesive was prepared, and its shear strength was horizontally compared with commercially available SPI adhesives, urea−formaldehyde adhesives, and other nonaldehyde adhesives. The performance of the novel SPI adhesive is comparable to or even superior to that of commercially available adhesives.

2. MATERIALS AND METHODS

2.1. Materials. The 400 × 400 × 1.5 mm poplar wood boards were procured from a local company. SPI with a protein content exceeding 85% was supplied by Yuwang Ecological Food Co., Ltd. (Shandong, China). Kraft lignin was obtained from Tianjin Wood Elf Biotechnology Co., Ltd. Chemicals including NaOH (99%), sodium chloroacetate, trimethylolpropane triglycidyl ether (TTE, 99%), 1,6-hexanediol diglycidyl ether (HDE, 99%), 3,4-epoxycyclohexanecarboxylate (ECM, 99%), glycerol triglycidyl ether (GTE, 99%), and others were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Glycerol propoxylate triglycidyl ether (GPTE, 99%) was sourced from Zhengzhou Converge Chemical Co., Ltd. Triglycidylamine (TGA) was prepared in the lab according to our previous report,[11] and the detailed

preparation process is described in the Supporting Information. All chemicals used in this experiment were ACS grade.

2.2. Preparation of Carboxymethylated Lignin (CML). Kraft lignin (50 g) was dissolved in 100 mL of 1.5 mol/L NaOH solution, followed by the addition of 50 g of sodium chloroacetate. The reaction system was heated at 60 °C for 2 h, and then the pH of the mixture was adjusted to 4.0 using 5% (v/v) H_2SO_4. The precipitated solid was collected, washed with deionized water until pH neutral, and then transferred to a 60 °C oven until a constant weight was achieved. The final carboxymethylated lignin (CML) product was collected.

2.3. Preparation of Soy Protein-Based Adhesives. Kraft lignin or CML was added to 42 g of distilled water. The pH was adjusted to 9 using a 10 wt % NaOH solution, and the mixture was thoroughly stirred, followed by the addition of soy protein (10 g) under vigorous stirring. Different cross-linking agents were then introduced, and the mixture was stirred at 1200 rpm for 10 min. The adhesives are referred to as SPI-#lig or SPI-#CML, wherein # represents the weight percentage of lignin or CML, respectively, based on the weight of SPI. The formulations for each adhesive with different lignin content and adhesives with different cross-linking agents are listed in Tables 1 and 2, respectively.

Table 1. Formulations of Adhesives with Different Lignin Contents

	SPI	Lignin	CML	TGA	DI water
neat SPI	10	-	-	1.7	42
SPI-5Lig	10	0.5	-	1.7	42
SPI-10Lig	10	1	-	1.7	42
SPI-15Lig	10	1.5	-	1.7	42
SPI-5CML	10	-	0.5	1.7	42
SPI-10CML	10	-	1	1.7	42
SPI-15CML	10	-	1.5	1.7	42

2.4. Preparation and Characterization of Engineered Boards. Three layers of poplar veneers were stacked together with their grain directions perpendicular to each other. Adhesive samples were uniformly applied between every two layers of veneers using a wool brush, ensuring a controlled application amount of 200 ± 10 g/m². The three overlaid layers of veneers were loaded into a flat vulcanization press and

Table 2. Formulations of Adhesives with Different Lignin Contents

	SPI	CML	cross-linking agent	cross-linking agent mass	DI water
SPI-HDE	10	1	HDE	1.7	42
SPI-ECM	10	1	ECM	1.7	42
SPI-GTE	10	1	GTE	1.7	42
SPI-GPTE	10	1	GPTE	1.7	42

hot-pressed at 120 °C and 1.0 MPa pressure for 9 min to form the composite engineered board. The cured composite boards were stored at room temperature for 24 h. The engineered boards were cut into several specimens of 100×25 mm (with a bonded area of 25×25 mm) for subsequent testing.

2.5. Characterizations. The viscosity of the adhesive mixture was measured using a plate rheometer (RSO, Brookfield, WI) with a shear rate ranged from 0.01 to 300 s^{-1} at room temperature. The shear strength of the adhesive was determined in strict accordance with the methods outlined in the Chinese National Standard (GB/T17657-2013). Specimens were immersed in water at 63 ± 3 °C for 3 h, followed by a 10 min air-drying period, and tensile testing was conducted with a universal testing machine (maximum capacity of 2 kN) at a rate of 10 mm/min to afford the wet shear strength. Each result was calculated by averaging six replicates. The wood fracture rate was obtained using an observation standard method (LYT 2720-2016) by calculating the ratio of the area of the wood fracture surface to the overall area of glue section of the specimen after testing.

The prepared adhesive was dried in a 105 °C oven to a constant weight and then mixed with potassium bromide to prepare pressed pellets. Fourier transform infrared spectra were obtained (IR Tracer-100, Shimadzu, Japan) in the range of 4000−400 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired with an AVII Bruker 400 MHz spectrometer at 25 °C using DMSO-d_6 as solvent.

Approximately 20 ± 2 mg of completely dried sample was taken for thermogravimetric analysis using a thermal gravimetric analyzer (Linseis TGA PT100, Linseis, Germany) under a N$_2$ atmosphere (flow rate: 20 mL/min) at a heating rate of 10 °C/min to 800 °C to determine the thermal degradation behavior, the residual rate, and moisture uptake.

The adhesive mixture was transferred to sterile Petri dishes and placed in a controlled environment at a constant temperature of 25 ± 2 °C with 80% relative humidity. The status was recorded to assess the antimicrobial and mold-resistant properties of the adhesive over time.

The cross-linked adhesive was ground into a powder with a 100-mesh size. The as-prepared powder (1.5 g) was added to 150 mL of DI water, and then the mixture was boiled for 3 h and filtered. The volume and weight of the powder before and after the boiling process were recorded as v_1, m_1 and v_2, m_2 (after drying), respectively. The moisture uptake rate (M_r) and the residual rate (R_r) were calculated using eqs 1 and 2, respectively.

$$M_r = \frac{v_1}{v_2} \times 100\% \tag{1}$$

$$R_r = \frac{m_1}{m_2} \times 100\% \tag{2}$$

The dried adhesive block was subjected to an external flame (alcohol lamp) for 30 s. Afterward, the alcohol lamp was removed, and the burning behavior of the adhesive block was recorded through video documentation. This procedure aimed to assess the flammability characteristics of the adhesive material.

3. RESULTS AND DISCUSSION

3.1. Structural Changes of Lignin after Carboxylation. Examination of the molecular structure and functional groups in lignin provides valuable insights into its chemical composition and cross-linking efficiency. Structural changes of lignin after carboxylation were monitored by NMR and FTIR (Figure 2a−c). ^{1}H NMR also confirmed the presence of CH$_2$COOH in the lignin skeleton. The peak at 3.38 ppm in Figure 2b corresponds to the proton in CH$_2$ in the carboxymethyl group. The peaks at 1600, 1510, and 1454 cm^{-1} in the FT-IR spectra correspond to the vibrational peaks of the aromatic ring skeleton[29] (Figure 2c). The bands in the range of 3300−3500 cm^{-1} are associated with the stretching vibrations of OH bonds. Compared to lignin, a decrease in
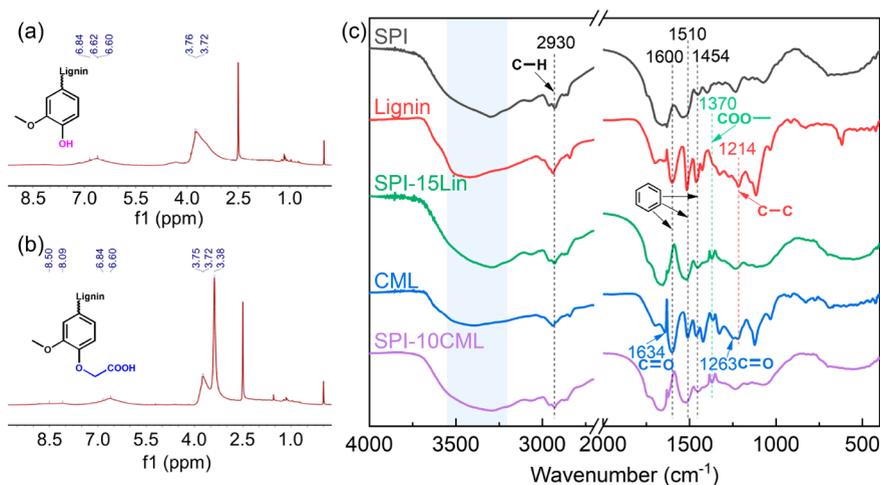
Figure 2. Functionality changes of lignin and CML. (a, b) NMR and (c) FTIR spectra of raw lignin and CML.
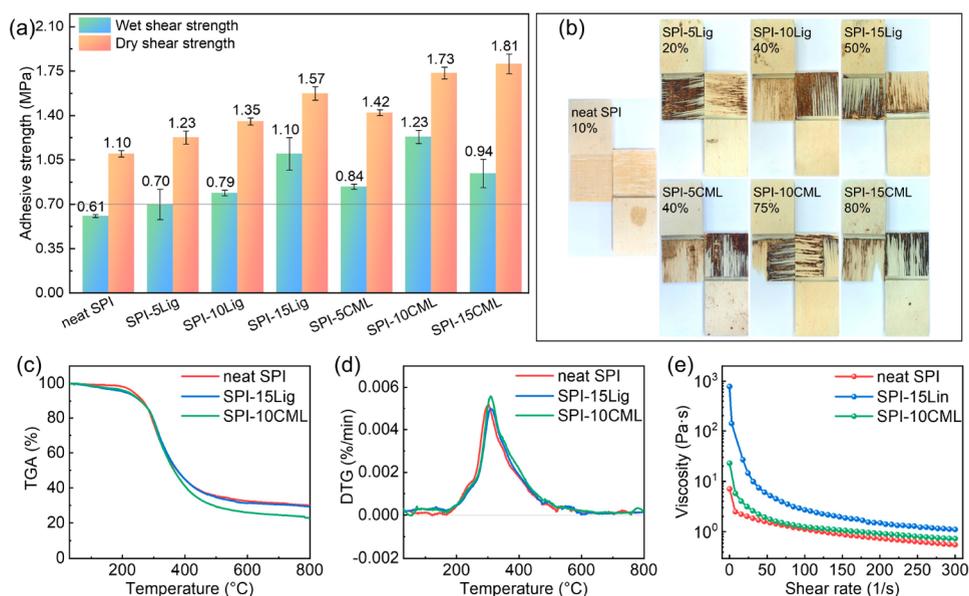
Figure 3. (a) Shear strengths and (b) wood fracture rate of plywood glued with different lignin-modified adhesives. (c-d) TG and DTG curves and (e) viscosity of different adhesives.

peak intensity at these regions for CML indicates the consumption of hydroxyl groups in lignin. Additionally, a new peak appears at 1263 cm^{-1} corresponding to the stretching vibration of C=O bonds in CML, confirming the successful carboxymethylation of lignin.[29] The enhancement of the stretching vibration peak of the benzene ring skeleton at 1600 cm^{-1} is also related to the introduction of carboxyl groups in the para position. Furthermore, the stretching vibration peak at 1370 cm^{-1} in both CML and adhesive is associated with COO$^-$ groups.[11]

3.2. Shear Strength and Thermostability of Plywood with Lignin-Modified Adhesives. The dry and wet shear strengths of plywood glued with as-prepared adhesives were recorded to evaluate the effect of lignin on the performance of soy protein-based adhesives (Figure 3). Notably, the addition of raw lignin (Figure 3a) gradually improved both the wet and dry shear strength of the plywood, and the strengths increased along with higher lignin loading, reaching 1.10 MPa (wet strength) and 1.57 MPa (dry strength) when using 15% raw lignin. This is presumably because the employment of lignin introduced more active sites (such as phenolic OH) to react with the cross-linking agent and form more inter/intra-hydrogen bonds (groups including OCH$_3$, OH, etc.). Low pH limited the complete dissolution of lignin particles in the adhesive, resulting in low shear strength of the adhesive, especially in wet shear strength.

In addition, carboxylation of lignin further improves the shear strength of those adhesives, reflected by the significantly higher wet/dry shear strengths which reached the maximum value to 1.23 MPa (wet shear strength) and 1.73 MPa (dry shear strength) when using 10% of CML. Additional formation of the amide/ester bonds between COOH (in CML) and NH$_2$ or OH (in soy protein) accompanied by extra hydrogen bonding and van der Waals force together contributed to the rise in shear strengths when employing CML in the adhesives. Higher CML loading yielded the opposite effect on the wet shear strength, which dropped to 0.94 MPa at a CML content of 15% albeit the dry shear strength slightly increased, likely because the inherent heterogeneity of lignin in the system

created difficulties for the coating progress. The changes in the tensile strength are in agreement with the wood fracture rate, evidenced by the increasing fracture rate from 10% (neat SPI) to 50% (SPI-15Lig), which further improved to 75−80% when employing 10%−15% CML in the adhesive (Figure 3b). SPI-15Lig and SPI-10CML were used to further evaluate the performances in the following tests.

Introduction of lignin or CML did not significantly alter the profiles of the TG and DTG curves of different adhesives, which all presented two major degradation stages, primarily including (i) the loss of low-molecular-weight compounds such as CO$_2$, water, and other volatile products ranging from room temperature to around 200 °C, and (ii) the corruption of the network and the breakage of most of the chemical linkages from 200 to 500 °C (Figure 3c,d). In addition, viscosity of the lignin-modified adhesives was recorded, as it is a critical index reflecting the coating or painting ability of adhesives during the plywood manufacturing progress, which is usually located around 5−25 Pa·s (Figure 3e). Incorporation of 15% raw lignin or 10% CML significantly increased the zero-shear viscosity to 781.5 Pa·s and 22.9 Pa·s, respectively, which is far higher than that of the neat SPI adhesive (7.0 Pa·s) presumably because of (i) the formation of more hydrogen bonding between the polar functional groups such as OH, NH$_2$, COOH, etc., in soy protein and lignin, (ii) the carboxyl groups of CML cross-linked with TGA to form new chemical bonds,[11] and (iii) the inherent hydrophobic nature of lignin.[14]

3.3. Mildew Resistance and Flame-Retardant Performances. As a nutrition-rich biomaterial, soy protein can easily mold which destroys the skeletal network of the protein,[15] producing gases including H$_2$S, CO$_2$, etc. Mold is known to convey brittleness to the adhesive, weaken the strength of plywood after hot-pressing, and shorten its storage period.[10] An antimildew test was conducted by storing the adhesives in a sealed chamber with 80% humidity at 25 °C, and the appearance of different lignin-modified adhesives were recorded to evaluate the mildew resistance. Apparently, adhesives without any lignin modification were eroded by mold in around 2 days; however, either 15% raw lignin of 10%
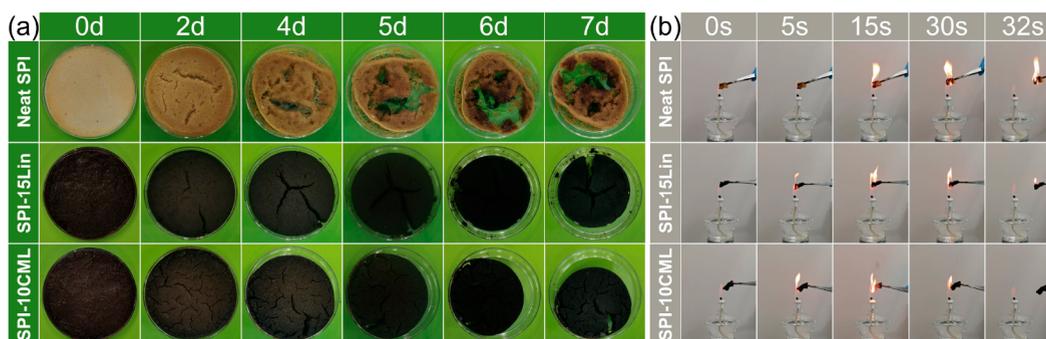
Figure 4. (a) Antimildew test and (b) flame-resistance test of different adhesives.
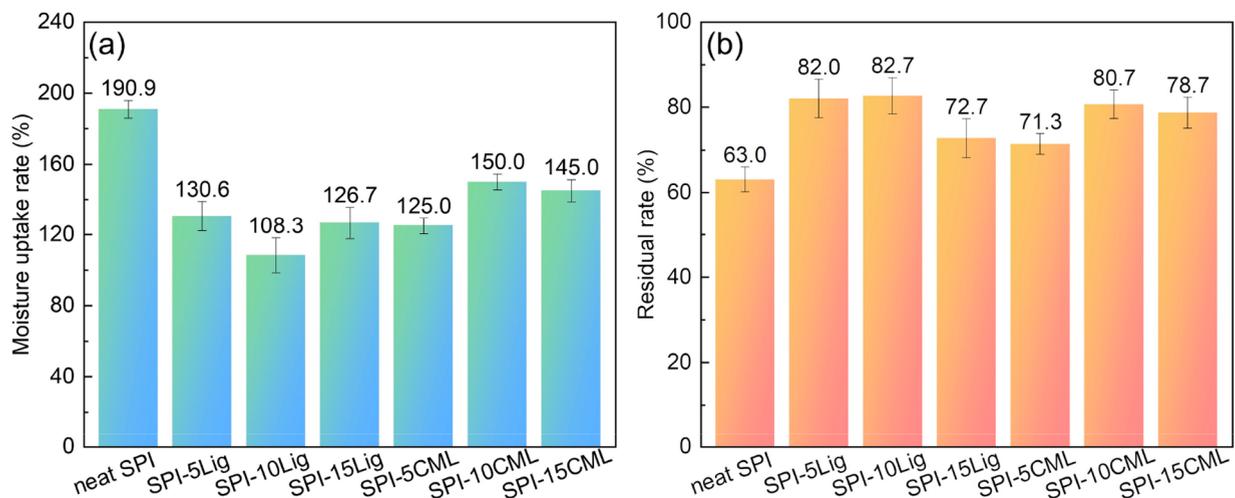
Figure 5. (a) Moisture uptake rate and (b) residual rate of different adhesivses.

CML can significantly prolong the storage time, and these samples showed no mildew even after 7 days (Figure 4a).

Carbon-rich lignin has a robust aromatic skeleton, and the polyphenol backbone is beneficial to improve the char carbon content during burning progress, thus delivering flame resistance to the adhesive. This is demonstrated when the neat SPI adhesive was immediately ignited and still burning at ∼32 s, while on the contrary, the flame of both SPI-15Lig or SPI-10CML ceased when moved from the lamp, implying the improved flame-resistance properties of these two adhesives due to the presence of the aromatic moiety of lignin (Figure 4b).

The residual rate and moisture taken rate reflected the structure changes and capacity of water resistance of those lignin-modified adhesives. Not surprisingly, employment of the hydrophobic lignin moiety can significantly reduce the moisture uptake rate from 190.9% (neat SPI) to 108.3% (SPI-10CML). Employment of other cross-linking agents showed a similar trend, presenting a moisture uptake rate around 125.0−150.0% (Figure 5a). Meanwhile, carbon-rich lignin also apparently improved the residual rate from 63.0% (neat SPI) to 82.0% and 82.7% (SPI-15Lig and SPI-10CML, respectively), despite the usage of different cross-linking agents (Figure 5b).

3.4. Effect of Different Epoxies on the Performance of Lignin-Modified Adhesives and Related Economic Analysis.
Compared to a vast number of different epoxy compounds (the cross-linking agents) in the market, the lab-made triepoxide TGA in this work holds the aspect of high-water solubility and reactivity in the fabrication of adhesives. From the perspective of economy, a plethora of commercialized and readily available epoxy compounds should be considered. Herein, in this work we screened several different commercial-available epoxies to evaluate their effect on the performance of the adhesives.

Not surprisingly, the wet shear strength of plywood glued with adhesives cured by diepoxides such as SPI-HDE and SPI-ECM apparently declined compared to that of the case using TGA (Figure 6), presumably because of the lower cross-linking density. In contrast, employment of triepoxides such as SPI-GTE and SPI-GPTE gradually improved the wet shear strength, reaching up to 1.12 and 1.17 MPa, respectively, which were both slightly lower than that of the sample with SPI-TGA (1.23 MPa) (Figure 6a). The differences might be associated with the inferior solubility/dispersity of these two triepoxides. A relatively lower wood fracture rate (ECM-55%) also reflected the lower cross-linking density compared to SPI-GTE (70%) and SPI-GPTE (85%, Figure 6c). On the other hand, all of these cured adhesives presented similar thermal degradation profiles, showing a $T_{5\%}$ (temperature corresponding to 5% weight loss) and $T_{30\%}$ (temperature corresponding to 30% weight loss) of 225 and 314 °C, respectively. All samples showed a T_{max} at 578 °C, and the residual rate ranged from 23.5% to 27.6% (Figure 6d,e). Because of the presence of the phenolic hydroxyl moiety in lignin, all samples still presented promising antimildew properties after being stored in a chamber with 80% relative humidity at 25 °C, showing no evidence of deterioration after 7 days (Figure 6b). Of
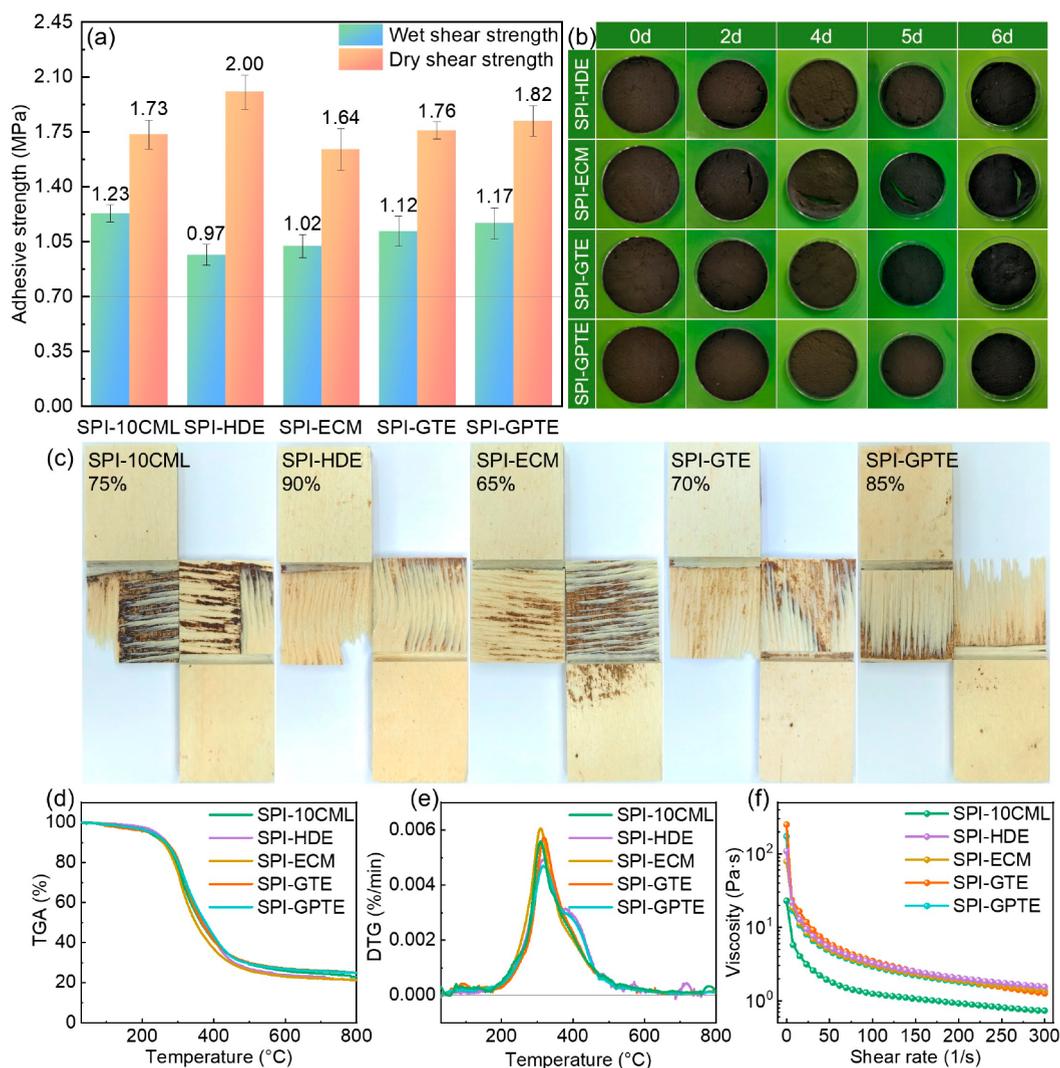
Figure 6. (a) Shear strengths, (b) antimildew test, and (c) wood fracture rate of plywood glued with different lignin-modified adhesives. (d, e) TG and DTG curves and (f) viscosity of the SPI-HDE, SPI-ECM, SPI-GTE, and SPI-GPTE adhesives.

particular significance is that the viscosity of SPI-10CML (in which water-soluble triepoxide TGA was used as the cross-linking agent) is much lower than that of samples that used other less-water-soluble epoxides (Figure 6f), again demonstrating the advantage of SPI-10CML in the coating progress.

Finally, we compared the performances of our adhesive in this work (Table 3) to commercialized urea glue and other soy protein-based adheisve. To our please, the SPI-10CML adhesive presented comparable or even improved perform-

Table 3. Performance Comparison

	commercial urea glue	commercial soy protein adhesive	SPI-10CML
wet shear strength (MPa)	1.14	1.18	1.23
dry shear strength (MPa)	1.54	1.69	1.73
curing temperature (°C)	120	120	120
Curing time (min)	120	15	9
pH	8.5	9.0	9.0
viscosity (MP·s)	29.0	21.1	22.9

ances, showing its promising practical applications, particular in the aspect of curing time (only ~9 min).

■ CONCLUSION

The current study presents a lignin-modified SPI-based artificial board adhesive, in which lignin is precarboxymethylated before introducing it into the system. Formation of additional amide and ester bonds between CML and SPI created a denser three-dimensional interpenetrating network structure. The dry and wet tensile strengths of the adhesive are enhanced from 1.10 and 0.63 MPa to 1.73 and 1.23 MPa, respectively, resulting in improvements of 157% and 195%. Additionally, the introduction of CML increases the carbon content of the adhesive, providing flame-retardant properties. In comparison to other epoxy cross-linking agents, the TGA significantly reduces the adhesive's viscosity, indicating its suitability for industrial spray applications. In conclusion, CML holds immense potential in the development of high-performance, high-strength, flame-retardant, and mold-resistant adhesives.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c00452.

Synthesis of triglycidylamine, capital analysis of adhesives, table of price and manufacturer information of raw materials, and table of formulations of adhesives with different lignin contents (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Zhen Fang − *Shandong Laboratory of Yantai Advanced Material and Green Manufacture, Yantai 264006, China; International Innovation Center for Forest Chemicals and Materials, Nanjing Forestry University, Nanjing 210037, China;* ⓞ orcid.org/0000-0001-7695-9427; Email: fangzhen@amgm.ac.cn

Yangbing Wen − *Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science & Technology, Tianjin 300457, China;* ⓞ orcid.org/0000-0001-6998-0869; Email: yangbingwen@tust.edu.cn

Authors

Changjiang Sun − *Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science & Technology, Tianjin 300457, China; Shandong Laboratory of Yantai Advanced Material and Green Manufacture, Yantai 264006, China;* ⓞ orcid.org/0000-0001-6623-8175

Fengxiang Cao − *Shandong Laboratory of Yantai Advanced Material and Green Manufacture, Yantai 264006, China*

Yecheng Xu − *Shandong Laboratory of Yantai Advanced Material and Green Manufacture, Yantai 264006, China*

Jiao Feng − *Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science & Technology, Tianjin 300457, China; Shandong Laboratory of Yantai Advanced Material and Green Manufacture, Yantai 264006, China*

Keyan Wang − *Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science & Technology, Tianjin 300457, China*

Complete contact information is available at:
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Author Contributions

Changjiang Sun: Data curation, writing - original draft. Yecheng Xu: Investigation. Jiao Feng: Validation. Zhen Fang: Writing - review and editing. Keyan Wang: Formal analysis. Yangbing Wen: Supervision. Fengxiang Cao: Resources, methodology.

Notes

The authors declare no competing financial interest.

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