

Development of a Renewable Hybrid Resin System by Blending Isocyanate with Novolac Phenolic Resins

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Abstract

The objective of this study was to develop a performance-competitive bio-based hybrid resin system composed of methylene diphenyl diisocyanate (MDI) resin and novolac phenol-formaldehyde (PF) resin for engineered wood panel manufacturing. A novolac PF resin and a bio-oil-modified PF resin were blended with MDI at weight ratios of PF to MDI of 85:15, 75:25, 50:50, and 25:75, respectively. The obtained hybrid resins were examined with Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA), and evaluated as plywood binders. The results indicated that the gel times and viscosities of hybrid resins were closely related to the weight ratio of PF resin to MDI. At a ratio lower than 75:25, the viscosities of hybrid resins were appropriate for plywood application. FTIR results showed some reactions between the novolac PF resin and MDI. TGA results showed that reacting novolac PF resin with MDI resin possibly increased the thermal stabilities of hybrid resins in the temperature range of 150°C to 300°C. Panel performance tests showed that blending novolac PF resin with MDI increased both the dry and the wet bonding strength of panels at the optimal ratio of 50:50. Replacing phenol with bio-oil of the hybrid resin had the trend of reducing the hybrid resin gel time and increasing panel dry and wet bonding strength.

Methylene diphenyl diisocyanate (MDI) resin is an important adhesive used in the wood panel industry because of its good bonding performance and water resistance. The actual resin used in panel manufacturing is polymeric MDI composed of a mixture containing a certain proportion of MDI monomers and polyphenyl polymethylene polyisocyanate (Mao et al. 2011). However, the issues of high cost and excessive permeability of MDI monomers into wood veneer, causing insufficiency of adhesive on the veneer surface, have restricted its application for veneer-based panels, such as plywood (Li et al. 2017).

Thermosetting phenolic resin, known as resol phenol-formaldehyde (PF) resin, is also an important binder used in the wood panel industry (Wan et al. 2017). The liquid PF resin contains a mixture of oligomers of PF reactants. When heated to high temperature (about 140°C), PF resin cures to form a cross-link structure with high heat resistance, high tensile strength, and high water and chemical resistance. However, the curing of PF resin is usually slow, resulting in lower hot-pressing efficiency. Moreover, as a petroleum-derived chemical, phenol is expensive and nonrenewable. Therefore, developing technologies for using alternative raw materials, such as biomass-derived phenols, is of high necessity (He et al. 2020).

Another important phenolic resin, known as novolac PF resin, is obtained first by reacting formaldehyde with an excess of phenol in the presence of acid catalysts. This

process produces a viscous or solid thermoplastic polymer. Novolac PF resin has a linear structure with several phenolic –OH groups attached to repeating units that are like normal –OH groups in polyether/polyester polyols (Yuan et al. 2014). It is cured with formaldehyde added later and is usually used for pressurized molding.

Based on the different characteristics of polymers, such as resol PF resin and MDI, they were designed and blended to develop a hybrid resin system to take advantage of both resins (Liu et al. 2016). Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) were extensively used to characterize the thermal properties of PF resin, MDI, and their hybrid resin systems (Mao and Shi 2012, Liu et al.

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2016). Nevertheless, because of the high chemical reactivity of MDI groups and the great differentiation in polarity between the MDI and PF resins, an emulsified MDI was designed to replace MDI to allow the reaction of resin mixtures to be more controllable (Miller and Rosthauser 2002). Still, this adjustment did not provide the resins with a good combination of proper storage life and high binding performance.

The pyrolysis of woody biomass produces a liquid bio-product called bio-oil (Li et al. 2013). As a renewable biomass resource, pyrolysis bio-oil is currently used as an energy source and a feedstock for chemical production (Mao and Shi 2012). Bio-oil contains water, sugars, alcohols, aldehydes, ketones, organic acids, and phenolic compounds with various molecular weights. The phenolic compounds in bio-oil are phenol and its oligomers with various numbers of phenolic rings (Kim 2015). Therefore, bio-oil is considered to be a potential source for chemical supply (Celikbag and Via 2015). In particular, phenolic compounds in bio-oil have various uses in the resin industry, for example, as an alternative phenol for phenolic resins for sustainable development purposes (Mao et al. 2018).

Although the applications of PF resin, MDI, and bio-oil have been extensively studied in recent years, limited reports have been found on resins composed of MDI with novolac PF resin and especially with bio-oil–modified novolac PF resin. As another type of phenolic resin, novolac PF resin with a linear structure is expected to be more compatible with MDI resin and does not cure at pure status. Its hydroxyl groups are likely to react with –NCO groups of MDI in the same way as polyols to form urethane bonds (–CO–NH–). In addition, novolac PF resin contains much less water, which is beneficial during reaction with MDI, leading to the formation of a uniform hybrid resin system of potential higher bonding strength and thermal stability. In this study, the characteristics and performance of hybrid resin systems composed of MDI and novolac PF resin with different blending ratios (weight basis) were investigated. The objective of this study was to develop a performance-competitive bio-based hybrid resin system with a reasonable operational procedure for engineered wood panel manufacturing.

Materials and Methods

Materials

In this study, chemicals such as phenol (99%), formaldehyde (37%), methanol (99%), and sulfuric acid (H_2SO_4) were obtained from the Sinopharm Group Co. Ltd (Beijing). Polymeric MDI with a 31.5 percent –NCO functional group was obtained from the Wanhua Chemical Group Co. Ltd (Yantai, China). This is a dark yellow liquid with a viscosity of 278 mPa/s at 25°C. Birch (*Betula* sp.) veneers with a thickness of 1.6 to 1.7 mm and a moisture content of 8 to 10 percent were obtained from a local plywood factory.

Bio-oil was produced from the pyrolysis of pinewood (Chinese pine) in an auger reactor (Li et al. 2013). The oven-dried pinewood particles with sizes of 16 to 20 mesh were pyrolyzed at 480°C under atmospheric pressure with retention times of 1 to 2 seconds. During the process, nitrogen was used at a flow rate of 100 to 150 cm^3/min to exclude oxygen from the system in the front of the feed hopper. After that, the crude bio-oil obtained was filtered by a charcoal filter to

remove solid residuals, and water was added to bio-oil to separate a water-rich layer from a water-insoluble fraction of the bio-oil. Then the water-rich layer was removed. The remaining water-insoluble fraction was mixed with methanol at a 1:1 weight ratio to give a clear solution. A certain amount of water was gradually added again to generate a precipitate that was viscous liquid with a dark color and was considered as a pyrolytic lignin fraction (phenol-rich) of bio-oil (Sukhbaatar et al. 2009). The extracted phenol-rich bio-oil was stored in sealed glass bottles in a refrigerator at 4°C to 5°C. The pH value, viscosity, and water content of the bio-oil were 5.8, 1,618 mPa/s, and 18.6 percent, respectively.

Preparation of novolac PF resins

The novolac PF resin with a ratio of formaldehyde to phenol of 0.9 was synthesized with phenol charged once and formaldehyde charged twice (F_1 and F_2). At the beginning, the calculated amount of phenol (235.0 g) was charged into a four-neck round-bottom flask equipped with a mechanical stirrer and a reflux condenser. The reaction mixture was heated to 95°C. Then the pH value of the mixture was adjusted to 2.5 with H_2SO_4 (10%), and F_1 (129.2 g) was charged into the flask. The mixture was maintained at 95°C for 60 minutes. Then F_2 (22.8 g) was charged into the flask. The mixture was maintained at 95°C for another 45 minutes. The synthesized novolac PF resin was then vacuum distilled at 120°C until most of the water was removed. The obtained PF resin was used as the control resin and marked as PF-C. The average molecular weight (M_n), water content, and free phenol content of the PF-C were 682.56, 10.8, and 3.7 percent, respectively.

The bio-oil–modified novolac PF resins were synthesized with 15 percent of phenol partially replaced by extracted phenol-rich bio-oil, based on the weight of phenol. The synthesis procedure of novolac PF resins was similar to that of PF-C resin. Bio-oil was charged together with the phenol. The synthesized bio-oil–modified PF resin was then vacuum distilled at 120°C until most water was removed. The PF resin obtained was marked as PF-B. The M_n , water content, and free phenol content of the PF-B were 664.03, 9.6, and 4.2 percent, respectively.

Preparation of hybrid resin systems

The hybrid resin systems were prepared under laboratory conditions by physically blending PF-C resin/PF-B resin with MDI at different weight ratios (85:15, 75:25, 50:50, and 25:75; Table 1). During the process, PF-C/PF-B resins were placed in a 250-mL beaker, and the MDI was added separately. Then the mixture was stirred thoroughly with a glass rod for about 5 minutes. The obtained hybrid resin systems were marked as PF-C-85, PF-C-75, PF-C-50, and PF-C-25 and PF-B-85, PF-B-75, PF-B-50, and PF-B-25 (Table 1).

Evaluation of resin properties

The viscosities of PF-C, PF-B, and hybrid resins were measured at 25°C in accordance with Chinese National Standard GB/T 14074-2017 (Standardization Administration of China [SAC] 2017) with a rotational Brookfield DVS+ viscometer (Brookfield Engineering Laboratories Inc., Middleboro, Massachusetts). The gel times of the resins were measured at 100°C (boiling water) in accor-

Table 1.—Composition of the resin systems.^a

Resin code	Resin composition		
	PF-C	PF-B	MDI
PF-C	100	—	—
PF-C-85	85	—	15
PF-C-75	75	—	25
PF-C-50	50	—	50
PF-C-25	25	—	75
PF-B	—	100	—
PF-B-85	—	85	15
PF-B-75	—	75	25
PF-B-50	—	50	50
PF-B-25	—	25	75
MDI	—	—	100

^a PF = phenol-formaldehyde; MDI = methylene diphenyl diisocyanate.

dance with Chinese National Standard GB/T 14074-2017 (SAC 2017). The gel time of resin affects the hot-pressing schedule and the panel production efficiency. Normally, shorter gel time results in faster hot pressing and higher production efficiency. The solid content was measured by oven-drying the resin sample at 125°C for 2 hours with three replicates.

Fourier-transform infrared spectroscopy

Fourier-transform infrared (FTIR) spectroscopy of resins was conducted using a Bruker TENSOR II spectrophotometer (Bruker Optik GmbH, Ettlingen, Germany) to monitor the FTIR spectrum change of hybrid resin at different weight ratios of PF to MDI. During the test, all the resin samples were placed in a convective drying oven at 120°C for 3 hours. The solid resin specimens were located in the observation stage of the spectrophotometer. FTIR spectra of a total of 64 scans for each sample were recorded in the wavelength range of 4,000 to 600/cm.

TGA

TGA of resins was carried out with a TA Q50 analyzer (TA Instruments, New Castle, Delaware) to characterize the thermal stabilities of PF resins and cured hybrid resins. During the test, all the resin samples were placed in a convective drying oven at 120°C for 3 hours. Specimens were placed in alumina crucibles and heated from 25°C to 600°C at a heating rate of 10°C/min. The flow rate of nitrogen purge gas was 20 mL/min. TG curves of weight loss and derivative weight loss (DTG) were plotted.

Panel manufacturing

Three pieces of birch veneers were cut in an end-matched manner for plywood manufacturing. The plywood with dimensions of 300 by 300 mm was manufactured using a laboratory hot press (XinXieLi Machine Manufacturing Co. Ltd, Suzhou, China). The resin application rate was 220 g/m² (double glue line). The resins were applied uniformly on both sides of the middle veneer with a brush. The hot press time, temperature, and pressure were 6 minutes, 125°C, and 1.1 MPa, respectively. Two panels were made for each resin formulation. After pressing, the plywood panels were conditioned at 20°C and 60 percent relative humidity for 7 days.

Measurement of the bonding strength

The bonding strength was measured by tension test in accordance with Chinese National Standard GB/T 17657-2013 (SAC 2013). Six specimens with dimensions of 100 by 25 mm were cut from each panel to make a total of 12 specimens for each resin formulation. Among them, six specimens were randomly selected and tested for dry bonding strength, and the remaining six specimens were tested for wet bonding strength. For wet bonding strength, specimens were immersed in boiling water for 4 hours, dried in an oven at 63°C for 18 hours, and then immersed into the boiling water again for 4 hours. The specimens were then cooled in water at 25°C and tested with a CMT 4104 universal testing machine (MTS Systems Corporation, Eden Prairie, Minnesota). The test results were averaged with standard deviations provided. The wood failure percentage was measured and recorded.

Statistical analysis

Means and standard deviations of the data obtained were calculated. One-way analysis of variance and Duncan mean comparison tests with SPSS version 13.0 software (IBM, Chicago, Illinois) were used to determine the differences among different resins.

Results and Discussion

Resin physical properties

Viscosity, gel time, and solid content results of the resins are presented in Table 2. The viscosities of the hybrid resins increased with PF-C and PF-B resin content (from 278 mPa/s for MDI to 9,820 mPa/s for PF-C-85 resin and 9,430 mPa/s for PF-B-85 resin). The viscosities of PF-C and PF-B resins were very high (14,860 and 15,940 mPa/s, respectively). This could be attributed to the low water content in PF-C and PF-B resins (10.8% and 9.6%, respectively) and the hydrogen bonding interaction of —OH groups of phenol compounds (Ahn et al. 2003). Based on the results (Table 2), there might be difficulties in the application of resins on veneer surfaces for plywood/laminated veneer lumber manufacturing when the weight ratio of PF-C and PF-B resins to MDI is higher than 75:25. According to production practice experience, the applicable viscosity of a plywood resin is usually in the range of 1,000 to 1,500 mPa/s before resin mixing. Because of this, PF-B and PF-C were not used in bonding plywood in the following tests.

Table 2.—Physical properties of the resins.^a

Resin code ^b	Viscosity (mPa/s)	Solid content (wt%)	Gel time (s)
PF-C	14,860	85.6	—
PF-C-85	9,820	87.3	>300
PF-C-75	6,299	88.8	218
PF-C-50	4,185	92.8	108
PF-C-25	1,940	96.2	149
PF-B	15,940	86.4	—
PF-B-85	9,430	88.0	>300
PF-B-75	6,688	89.9	187
PF-B-50	4,090	93.2	96
PF-B-25	1,848	96.7	125
MDI	278	100	>300

^a Missing data are due to novolac phenol-formaldehyde resin not being able to cure under the gel time test condition.

^b PF = phenol-formaldehyde; MDI = methylene diphenyl diisocyanate.

The solid contents of PF-C, PF-B, and MDI were 85.3, 86.2, and 100 percent, respectively. This resulted from the fact that increasing the content of PF-C and PF-B resins decreased the solid contents of the PF-C and PF-B hybrid resin system from 100 to 87.3 percent and from 100 to 88.0 percent, respectively. The higher solid content level of resins, as noted above, resulted in resins with higher viscosity and brought less water into the veneers.

The curing of MDI needs enough reactive groups or moisture that can react with the $-NCO$ group. When placed in the air alone, MDI cures slowly with moisture, as shown above (Table 2). However, if applied to a wood surface with a certain moisture content, MDI could react readily with $-OH$ groups as well as moisture in wood and cure in a short time. For PF-C hybrid resins, increasing the content of PF-C resin first decreased the gel time (from 149 to 108 s) and then increased it quickly (from 108 to >300 s). The decrease of gel time might be attributed to the reaction between $-NCO$ and $-OH$ groups. At a weight ratio of 50:50, the $-OH$ groups in PF-C resin appeared to react fully with the $-NCO$ groups in MDI (see FTIR results in Fig. 1). This could promote resin curing and result in a shorter gel time. As a typical thermoplastic polymer, PF-C resin was not able to cure at any temperature. Therefore, if more PF-C resin was blended with MDI, the obtained hybrid resin systems became more difficult to cure, resulting in a longer gel time. This explains the fact that increasing the amount of PF-C of hybrid resin increased the gel time.

For PF-B hybrid resins, the trend was similar. At a weight ratio of PF-B to MDI of 50:50, the obtained hybrid resin system (PF-B-50) had the shortest gel time, indicating that $-NCO$ groups reacted with enough $-OH$ groups and moisture. Further increasing the amount of PF-B of hybrid resin increased the gel time.

Concerning the influence of bio-oil, the gel times of PF-B hybrid resins were shorter than those of PF-C hybrid resins. The possible reason might be that the incorporation of phenol-rich bio-oil into PF resin brought in phenols and polyphenols with various numbers of phenolic rings with a

hydroxyl group (Sukhbaatar et al. 2009). Some of these phenolic compounds had a higher molecular weight than phenol and might serve as cross-linking agents to promote resin curing. Generally, replacing phenol with bio-oil had the trend of reducing the resin gel time.

FTIR analysis

The FTIR analysis of MDI, PF-C, and hybrid PF-C resin systems is shown in Figure 1. The characteristic bands of the aromatic ring from both MDI and PF-C resins were observed in the range of 1,590.4 to 1,451.8/cm (Liu et al. 2016). The band at 3,272.1/cm was attributed to $-OH$ groups of phenolic compounds from PF-C resin (Aslan et al. 2015). This band disappeared when the weight ratio of PF-C to MDI was lower than 75:25, indicating that $-OH$ was consumed in reactions with $-NCO$ groups. The band feature of the $-NCO$ group was observed at 2,249.9/cm. The remarkable difference among the hybrid resins and the PF-C resin was that the $-NCO$ groups presented in some hybrid resins, such as PF-C-50 and PC-C-25, which means that there were some isocyanate compounds left in the MDI, PF-C-25, and PF-C-50 resins (Li et al. 2020).

Figure 1 also displays the difference in the reaction of $-OH$ and $-NCO$ groups in hybrid resins with different weight ratios. As observed above, at a weight ratio of PF-C to MDI of 50:50, there were some residual isocyanate compounds left in the hybrid resin system. At a weight ratio of PF-C to MDI of 75:25, the characteristic peak of the $-NCO$ group became almost invisible, which meant that the reaction was completed and few $-NCO$ groups were left. This provided a perspective to compare the resin system of PF-C resin to MDI. It was obvious that there were variable $-NCO$ groups left in the resin systems of different weight ratios of PF-C to MDI. As the ratio of PF-C to MDI increased in the hybrid resin systems, the peak intensity of the $-NCO$ groups became weaker. This indicated that a higher weight ratio of PF-C to MDI promoted the reaction of MDI and PF resin.

The FTIR analysis of MDI, PF-B, and hybrid resins is shown in Figure 2. The characteristic bands of these resins

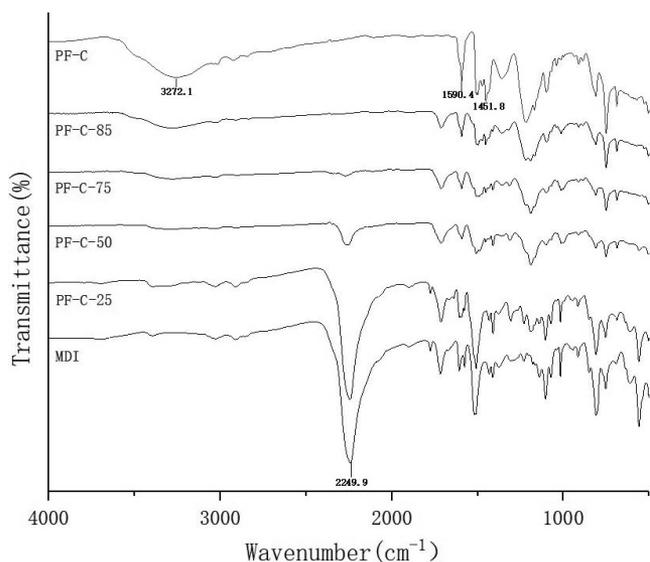


Figure 1.—Fourier-transform infrared spectra for phenol-formaldehyde (PF)-C, methylene diphenyl diisocyanate (MDI), and hybrid resins.

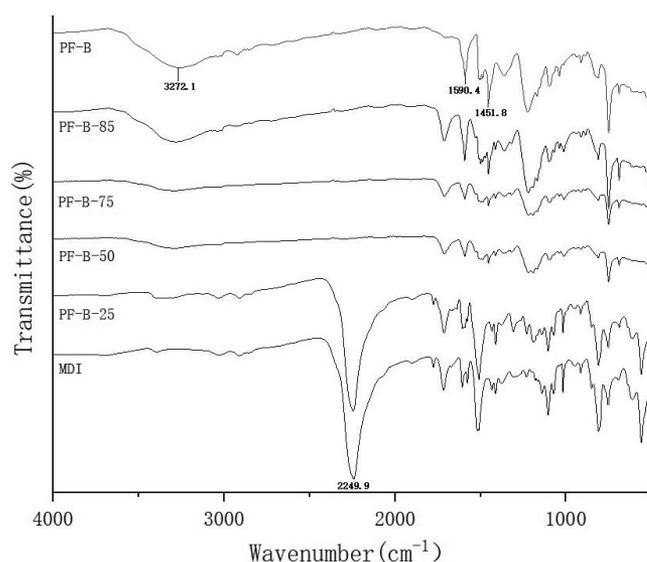


Figure 2.—Fourier-transform infrared spectra for phenol-formaldehyde (PF)-B, methylene diphenyl diisocyanate (MDI), and hybrid resins.

were similar to those presented in Figure 1. The difference was that, in Figure 1, at a weight ratio of PF-C to MDI of 50:50, there was a small peak of residual $-NCO$ group in the hybrid resin system. But in Figure 2, at the same weight ratio, the peak of the $-NCO$ group disappeared. This indicated that when bio-oil was incorporated into PF resin, the reaction between MDI and PF-B resin was completed at a lower ratio of PF-B to MDI, showing that in PF-B there were more hydroxyl groups than in PF-C.

TGA

The TG and DTG curves of the MDI, PF-C, and hybrid resin systems are shown in Figures 3 and 4, and the calculation of weight loss of the resins is shown in Table 3. From room temperature to 600°C, two different weight loss ranges were observed for MDI and PF-C-25 resins, while the TG curves of PF-C-50, PF-C-75, PF-C-85, and PF-C resins were much smoother with multiple smaller weight loss ranges indicated by DTG curves (Fig. 4). This showed that MDI and PF resin were two different resins or materials. Mixing MDI and PF resin together improved the thermal stability of both. As shown in Table 3, the first weight loss range of MDI and PF-C-25 resin occurred between about 150°C and 300°C, which had a weight loss of about 59 and 51 percent, respectively. Also, within this temperature range (150°C to 300°C), the weight losses of PF-C-50, PF-C-75, PF-C-85, and PF-C resins were 23, 36, 44, and 48 percent, respectively. Therefore, at a lower temperature range (150°C to 300°C), blending MDI with PF-C resin increased the thermal stability of MDI at various levels. Among all the resins, PF-C-50 appeared to have the highest thermal stability at a temperature below 300°C. It appeared that the reaction of $-NCO$ groups in MDI with $-OH$ groups in PF-C resin increased the thermal stability of the cured hybrid resins.

At the second weight loss range from 300°C to 600°C, MDI and PF-C-25 resin had a weight loss of about 18 and 22 percent, respectively, while the weight losses of PF-C-50, PF-C-75, PF-C-85, and PF-C resins were 44, 36, 30, and 24 percent, respectively. The possible reason might be that blending MDI with PF-C resin increased the thermal stability of MDI so that the second weight loss range of the hybrid resins was postponed due to higher temperature. The residual weight percentages were 23, 27, 32, 28, 26, and 28 percent for MDI, PF-C-25, PF-C-50, PF-C-75, PF-C-85, and PF-C resins, respectively. Among these resins, PF-C-50 had the lowest weight loss percentage, which confirmed that the reaction of $-NCO$ groups in MDI resin with $-OH$ groups in PF-C resin increased the thermal stability of the cured hybrid resin systems.

The TG and DTG curves of MDI, PF-B, and hybrid MDI/PF-B resins are shown in Figures 5 and 6, and the results of weight loss of the resins are shown in Table 3. The degradation temperature range and weight loss range were similar to those of MDI, PF-C, and hybrid MDI/PF-C (Figs. 3 and 4). Blending MDI with PF-B resin increased the thermal stability of resin systems at various levels. According to the TG result, PF-B-50 resin appeared to have the highest thermal stability.

Comparing the TGA results of PF-C and PF-B resins, although the final remains of these two resins were similar (28% and 30%, respectively), in the first weight loss range (from 150°C to 300°C), the weight loss of PF-C resin (48%) was obviously higher than that of PF-B resin (38%),

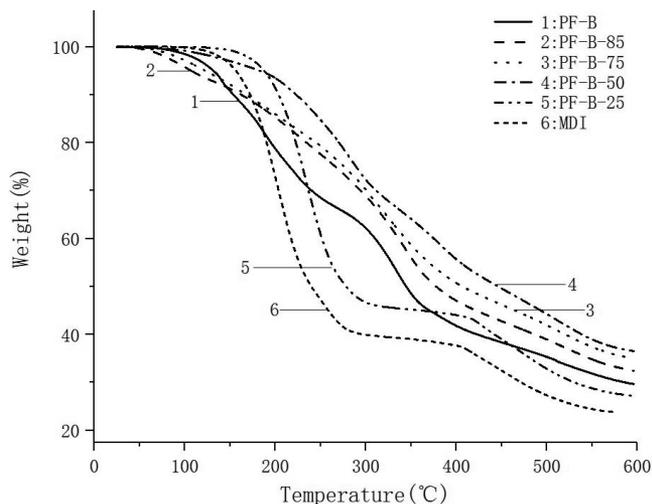


Figure 3.—Thermogravimetric curves of phenol-formaldehyde (PF)-C, methylene diphenyl diisocyanate (MDI), and hybrid resins.

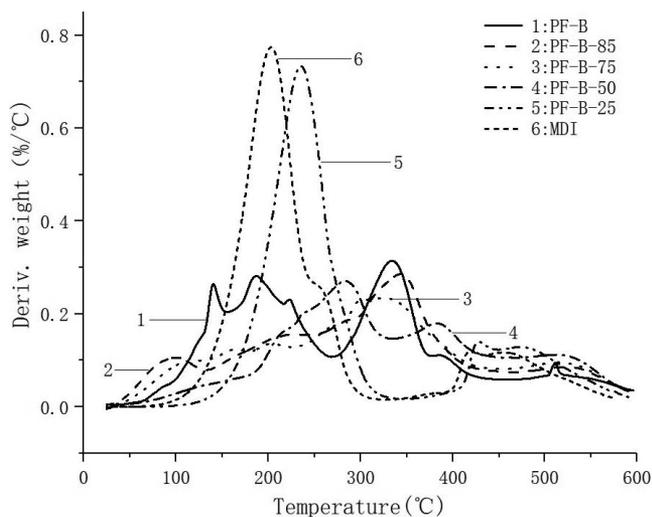


Figure 4.—Weight loss and derivative weight loss curves of phenol-formaldehyde (PF)-C, methylene diphenyl diisocyanate (MDI), and hybrid resins.

Table 3.—Responses of methylene diphenyl diisocyanate (MDI), phenol-formaldehyde (PF)-C, PF-B, hybrid PF-C, and hybrid PF-B resins by thermogravimetric analysis (TGA).

Resin code	Weight loss at different temperature ranges (%)		Residual percentage at the end of TGA (%)
	150°C–300°C	300°C–600°C	
PF-C	48	16	28
PF-C-85	44	26	26
PF-C-75	36	28	28
PF-C-50	23	42	32
PF-C-25	51	22	27
PF-B	38	25	30
PF-B-85	31	29	32
PF-B-75	30	29	34
PF-B-50	28	35	36
PF-B-25	53	20	27
MDI	59	18	23

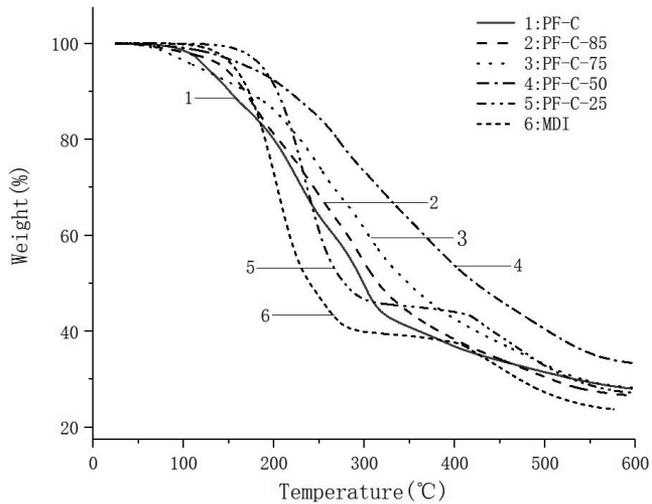


Figure 5.—Thermogravimetric curves of phenol-formaldehyde (PF)-B, methylene diphenyl diisocyanate (MDI), and hybrid resins.

probably indicating that incorporating bio-oil into PF resin increased the thermal stability of PF resin at this temperature range. Also, at the same weight ratio of PF to MDI, the residual weight percentages of PF-B hybrid resins were higher than those of PF-C hybrid resins, indicating that incorporating bio-oil into PF resin increased the thermal stability of hybrid resin systems.

As a summary, by comparing Figures 3 to 6, blending novolac PF resin with MDI resin improved not only the thermal stability of MDI but also that of novolac PF resin, especially in the temperature range from 0°C to 300°C. Future research is needed to explain the reason for this.

Panel bonding performance

The bonding strength and wood failure of the resins were determined (Table 3). Both the dry and the wet strengths of MDI, PF-C-25, PF-B-25, PF-C-50, and PF-B-50 resins met the requirements of Standard GB/T 17657-2013 (SAC 2013)

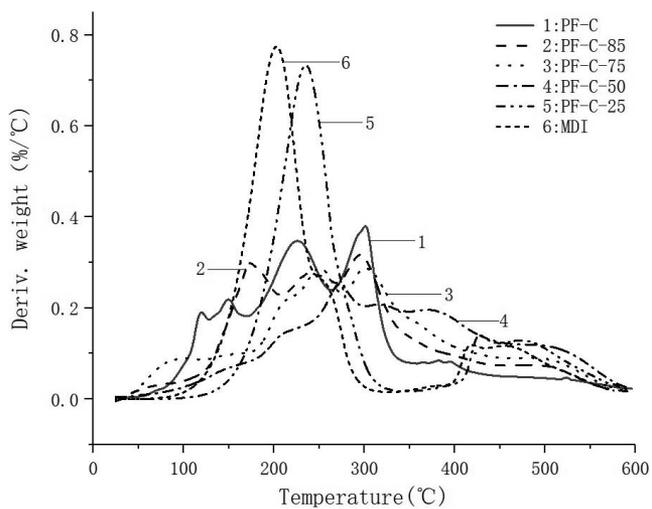


Figure 6.—Weight loss and derivative weight loss curves of phenol-formaldehyde (PF)-B, methylene diphenyl diisocyanate (MDI), and hybrid resins.

for outdoor applications (≥ 1.0 MPa for dry strength and ≥ 0.7 MPa for wet strength), and wood failure was decreased with the increase of novolac PF resin blend.

Direct use of MDI resin for bonding plywood in this study ran into some difficulties. When MDI resin was applied to the veneer surface, it penetrated into the veneer within 2 to 3 minutes, resulting in a deficiency of resin on the veneer surface (Li et al. 2020). Therefore, the veneers had to be hot pressed as soon as the MDI was applied. This could be realized in the lab but is not acceptable in factory production. Usually, after the resin is applied in a mill situation, at least 30 minutes is required before hot pressing. Data indicate that MDI resin did not yield the highest bonding strength and wood failure compared to hybrid resins (Table 4). This may show that for plywood applications, using MDI resin was not the best choice. Direct use of PF-C and PF-B resins for bonding plywood was not acceptable either (Table 4), as both of these resins are thermal plastic polymers and are not able to cure under hot pressing conditions.

However, designing the hybrid resin using MDI and novolac PF resin improved the bonding strength and increased the wood failure of plywood (Table 4). Compared with MDI resin, reacting 25 percent novolac PF resin with 75 percent MDI resin increased the dry bonding strength from 1.59 to 2.58 MPa and to 2.39 MPa and wet bonding strength from 1.28 to 2.24 MPa and to 2.06 MPa for PF-B and PF-C resins, respectively. It also improved the wood failure performance. Concerning the trend of adding PF novolac resin in the hybrid resin, as PF novolac resin increased, the dry and wet bonding strengths decreased, and so did the wood failure percentage, for both PF-C and PF-B resins. This shows that reacting a certain amount of novolac PF resin with MDI resin at least extended the MDI resin, improved MDI resin efficiency, and thus increased the bonding strength of hybrid resin, as assumed in the introduction. Based on the data obtained, it appears that blending 25 percent novolac PF resin was optimal for improving the bonding strength and wood failure. Further research is needed to explain the mechanism.

Table 4.—Bonding performance of the plywood.^a

Resin code ^b	Dry strength (MPa)	Wood failure (%)	Wet strength (MPa)	Wood failure (%)
PF-C	—	—	—	—
PF-C-85	0.88 (0.08) F	20 (6.32) D	0	0
PF-C-75	1.24 (0.14) E	50 (12.65) C	0.68 (0.05) F	0
PF-C-50	2.08 (0.10) C	100 (0) A	1.89 (0.08) C	100 (0) A
PF-C-25	2.39 (0.15) B	100 (0) A	2.06 (0.11) B	100 (0) A
PF-B	—	—	—	—
PF-B-85	0.56 (0.12) G	0	0	0
PF-B-75	0.87 (0.11) F	20 (14.14) D	0.71 (0.03) F	1.7 (4.08) D
PF-B-50	1.28 (0.08) E	100 (0) A	1.01 (0.09) E	50 (16.73) B
PF-B-25	2.58 (0.14) A	100 (0) A	2.24 (0.12) A	100 (0) A
MDI	1.59 (0.11) D	80 (14.14) B	1.28 (0.04) D	20 (16.73) C

^a Missing data are not available due to novolac phenol-formaldehyde resin not being able to cure under hot pressing condition and thus not able to bond wood veneers together. Values in the parentheses are sample standard deviations. Data in the same column with the same uppercase letter are not different at $\alpha = 0.05$.

^b PF = phenol-formaldehyde; MDI = methylene diphenyl diisocyanate.

Concerning the impact of bio-oil, blending 25 percent novolac PF resins, among which 15 percent of phenol was partially replaced by bio-oil, resulted in significant high dry bonding (2.58 vs. 2.39 MPa) and wet bonding (2.24 vs. 2.06 MPa) strengths, further increasing the percentage of novolac PF resin and thus the amount of bio-oil in the hybrid resin and decreasing both dry and wet bonding strength. This shows that adding a certain amount of bio-oil improved both the dry and the wet bonding strengths of plywood (Chaouch et al. 2014). Since the amount of bio-oil added was not a variable in this study, the optimal amount of bio-oil added in the hybrid resin needs further study. The reason that adding bio-oil improved the bonding strengths of plywood also needs further study.

Conclusions

In this study, novolac PF resin and bio-oil-modified PF resin were blended with MDI resin at weight ratios of 85:15, 75:25, 50:50, and 25:75. These resins were analyzed with FTIR and TGA and evaluated as plywood binders. The results are as follows: (1) The gel times and viscosities of hybrid resins were closely related to the weight ratio of novolac PF resin to MDI. At a ratio of 50:50, the obtained hybrid resins had the lowest gel time. At ratios lower than 75:25, the viscosities of hybrid resins were appropriate for plywood application. (2) FTIR results indicated that some reactions might occur within the mixture of novolac PF and MDI resins. This could help increase the cross-link density of cured hybrid adhesives, reduce the excessive permeability of MDI resin, and thus contribute to higher bonding strength. (3) TGA showed that blending novolac PF resin with MDI decreased weight losses of cured resins and increased thermal stabilities of both resins. Incorporating bio-oil into PF resin contributed to the thermal stability of the obtained hybrid resins. (4) Panel performance test results showed that blending PF with MDI resin at weight ratios of up to 50 percent increased both the dry and the wet bonding strengths compared with MDI. The optimal weight ratio of PF to MDI was 50:50 considering both the bonding strength and the production practice of plywood.

The route of developing a polyurethane type of resin via blending novolac PF with MDI resin shortened the press time of MDI resin, enhanced the thermal stability of both MDI and PF resin, improved panel performance, and provided a new way to incorporate renewable bioresources into resin applications. Future studies will be focused on the reaction mechanism between novolac PF resin and MDI, the microstructure of the bonding interface, and the optimization of the resin-forming procedure for plywood production.

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Literature Cited

- Ahn, D. S., S. W. Park, S. Lee, and B. Kim. 2003. Effects of substituting group on the hydrogen bonding in phenol-H₂O complexes: Ab initio study. *J. Phys. Chem. A* 107(1):131–139.
- Aslan, M., G. Ozbay, and N. Ayrimlis. 2015. Adhesives characteristics and bonding performance of phenol formaldehyde modified with phenol-rich fraction of crude bio-oil. *J. Adhes. Sci. Technol.* 457(24):2679–2691.
- Celikbag, Y. and B. Via. 2015. Characterization of residue and bio-oil produced by liquefaction of Loblolly pine at different reaction time. *Forest Prod. J.* 66(1):29–36.
- Chaouch, M., P. N. Diouf, A. Laghdir, and S. Yin. 2014. Bio-oil from whole-tree feedstock in resol-type phenolic resins. *J. Appl. Polym. Sci.* 131:596–602.
- He, M. M., D. D. Xu, C. G. Li, Y. Z. Ma, X. H. Dai, X. Y. Pan, J. L. Fan, Z. X. He, S. H. Gui, X. Y. Dong, and Y. F. Li. 2020. Cell wall bulking by maleic anhydride for wood durability improvement. *Forests* 11:367–378.
- Kim, J. S. 2015. Production, separation, and applications of phenolic-rich bio-oil—A review. *Bioresour. Technol.* 178:90–98.
- Li, Q., M. Li, C. Chen, G. M. Cao, A. Mao, and H. Wan. 2017. Adhesives from polymeric methylene diphenyl diisocyanate resin and recycled polyols for plywood. *Forest Prod. J.* 67(3–4):275–282.
- Li, Q., Y. F. Pang, X. S. Liu, E. H. Xi, A. Mao, and H. Wan. 2020. Addition of polyurethane foam wastes to polymeric diphenyl methane diisocyanate to improve plywood binder performance. *Forest Prod. J.* 70(3):262–267.
- Li, Q., P. H. Steele, F. Yu, B. Mitchell, and E. B. M. Hassan. 2013. Pyrolytic spray increases levoglucosan production during fast pyrolysis. *J. Anal. Appl. Pyrol.* 100:33–40.
- Liu, X. M., Y. Q. Wu, R. Shmulsky, Y. Luo, A. Wang, I. W. Chu, and H. Wan. 2016. Developing a renewable hybrid resin system. Part I: Characterization of co-polymers of isocyanate with different molecular weights of phenolic resins. *BioResources* 11(2):5299–5311.
- Mao, A. and S. Q. Shi. 2012. Dynamic mechanical properties of polymeric diphenylmethanediisocyanate/bio-oil adhesive system. *Forest Prod. J.* 62:201–206.
- Mao, A., S. Q. Shi, and P. H. Steele. 2011. Flakeboard bonded with polymeric diphenylmethanediisocyanate/bio-oil adhesive systems. *Forest Prod. J.* 61:240–245.
- Mao, A., W. T. Xu, E. H. Xi, Q. Li, and H. Wan. 2018. Evaluation of phenol-formaldehyde resins modified and blended with pyrolysis bio-oil for plywood. *Forest Prod. J.* 68(2):113–119.
- Miller, T. R. and J. W. Rosthauser. 2002. Aqueous mixed pMDI/phenolic resin binders for the production of wood composite products. US patent 6,416,696.
- Standardization Administration of China (SAC). 2013. Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels. GB/T 17657-2013. SAC, Beijing.
- Standardization Administration of China (SAC). 2017. Test methods of wood adhesives and resins. GB/T 14074-2017. SAC, Beijing.
- Sukhbaatar, B., P. H. Steele, and M. G. Kim. 2009. Use of lignin separated from bio-oil in oriented strand board binder phenol-formaldehyde resins. *BioResources* 4:789–804.
- Wan, H., J. Dahlen, A. Mao, L. Sites, A. Rowlen, G. Miller, B. McClendon, M. Liu, X. Liu, and D. Nicholas. 2017. Composite wood decking bonded with phenol-resorcinol formaldehyde and polyurethane adhesives after accelerated aging tests. *Forest Prod. J.* 67(1/2):112–119.
- Yuan, Z. S., Y. S. Zhang, and C. Xu. 2014. Synthesis and thermomechanical property study of novolac phenol-hydroxymethyl furfural (PHMF) resin. *RSC Adv.* 60(4):31829–31835.