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# Modification of urea-formaldehyde resin adhesives with blocked isocyanates using sodium bisulfite

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## Abstract

Polymeric 4-4 diphenyl methane diisocyanate (pMDI) was blocked with an aqueous sodium bisulfite solution to obtain water-dispersible blocked pMDI (B-pMDI) resin with different HSO<sub>3</sub>/-NCO mole ratios for the modification of urea-formaldehyde (UF) resin. Fourier transform infrared (FTIR) spectra of the B-pMDI resin clearly showed that all isocyanate groups of the pMDI resin were successfully blocked by sodium bisulfite. As the HSO<sub>3</sub>/-NCO mole ratio increased, the de-blocking temperature of the B-pMDI resin also increased. Two addition levels (1 and 3%) of the B-pMDI resin with different HSO<sub>3</sub>/-NCO mole ratios were mixed with UF resins and used as an adhesive for plywood. The gel time of the UF/B-pMDI resins decreased to a minimum at a mole ratio of 0.9 and then increased with the HSO<sub>3</sub>/-NCO mole ratio, and was consistent with the peak temperature (*T<sub>p</sub>*). However, as the HSO<sub>3</sub>/-NCO mole ratio increased, the viscosity of the modified UF resins by 1% B-pMDI resin addition slightly increased, whereas those of modified resins with 3% B-pMDI resin addition rapidly increased. The adhesion strengths of plywood bonded with the hybrid resins were greater for 1% B-pMDI resin addition than for 3% B-pMDI resin addition. Formaldehyde emission of

plywood bonded with the UF/B-pMDI resins significantly decreased up to 34% by the addition of B-pMDI resin at a mole ratio of 1.8. These results suggest that the modification of UF resins by mixing with water-dispersible B-pMDI resin can be a method for improving the water resistance and formaldehyde emission of UF resins for wood-based composites.

*Keywords: urea-formaldehyde resin, blocked isocyanate, sodium bisulfite, hybrid resin, plywood*

## 1. Introduction

Urea-formaldehyde (UF) resins are the most commonly used resins, with widespread application in the manufacture of wood-based composite panels, such as plywood, particleboard, and medium-density fiberboard. UF resins have advantages over other adhesives, such as easy handling, low cost, and good performance in panel products [1]. They also have a high reactivity, a clear glue line, and the absence of organic solvents and are non-flammable [2]. On the other hand, low moisture resistance and formaldehyde emission from wood-based composite panels are the two most important disadvantages of UF resins [3].

Compared with UF resins, polymeric 4-4 diphenyl methane diisocyanate (pMDI) based resins have positive characteristics such as good bonding performance, high water resistance, aging resistance, and no issues relating to formaldehyde emission. Furthermore, the hydroxyl groups in wood may react with the isocyanate group of pMDI resins to form a polyurethane bond and provide direct covalent linkages between the adhesive and wood [4]. Several works have analyzed wood-pMDI cure using different methods, such as differential scanning calorimetry (DSC) [5], infrared (IR) spectroscopy [6], and nuclear magnetic resonance (NMR) spectroscopy [7]. They found that the formation of biuret, polyuret, and polyurea are very common in wood-pMDI cure systems. However, the formation of urethane bonds was only detected when huge excesses of pMDI were used.

Unfortunately, these systems are very sensitive to moisture at room temperature before curing [8]. And, pMDI is not dispersible in water, because it is oil-borne. It is necessary to make pMDI resins compatible with water-based UF resins. Therefore, the blocking of isocyanate groups in pMDI resins is a solution to make pMDI resins dispersible in UF resins [9]. A blocked isocyanate is formed via a reaction between an isocyanate group (-NCO) and a

compound containing an active hydrogen atom to block the -NCO. This product has the advantage of a long shelf life because the active isocyanate groups are masked and protected [10]. Furthermore, it has a small amount of the isocyanate groups and requires a high temperature to de-block and to make the -NCO group free. The blocked isocyanate to be applied as a wood adhesive should be de-blocked at less than 100 °C because the core temperature in the wood-based composite production during hot-pressing is not much higher than ~100 °C (usually in the range 105 – 120°C). Among the various blocking agents, sodium bisulfite (NaHSO<sub>3</sub>) has special properties, such as a low de-blocking temperature (between 75 and 105 °C) [11 - 13], a low price, and no pollution problems, which makes it suitable for blocking pMDI resin.

Bisulfite-blocked isocyanate has been prepared by reacting isocyanate with aqueous solutions of sodium bisulfite to obtain water-dispersible blocked isocyanates. Several studies on bisulfite-blocked isocyanates have been reported, such as investigations on the blocking and de-blocking reaction [11], the preparation and characterization of bisulfite-blocked isocyanates [12, 13], and the de-blocking characterization of bisulfite-blocked isocyanate [14].

In order to improve the performance of UF resins, especially concerning their water resistance, pMDI is used to reinforce the characteristics of exterior-grade resins. To the author's knowledge, the first attempt of combining pMDI with formaldehyde based resin was done by spraying the melamine formaldehyde (MF) or phenol formaldehyde (PF) resin and pMDI in separate way [15]. Afterward, several researchers have attempted to fabricate such hybrid UF/pMDI resins, e.g., the addition range of pMDI from 15 to 40% into the UF resins [16 - 19]. The strength of wood composites bonded with UF/pMDI hybrid resin was improved because of the co-reaction between isocyanate groups and methylol groups of the UF resins

to form a number of urethane crosslinks [20,21]. It has been reported that a mixture of UF resin with pMDI has a higher degree of crystallinity compared to that of neat UF resin, and the mixture formed colloidal particles [21].

However, to date, there are only a few papers devoted to the development of blocked pMDI (B-pMDI) and combining the UF resins with the B-pMDI resin to improve the UF resin properties, particularly water resistance and formaldehyde emission. The present study was conducted to develop a B-pMDI resin with sodium bisulfite and to evaluate the adhesive performance of the hybrid UF/B-pMDI resin adhesives in plywood manufacturing. Furthermore, this paper describes the preparation and characterization of B-pMDI resins.

## 2. Experimental procedure

### 2.1. Materials

Technical-grade urea granules (99%), formaldehyde (37% HCHO), and aqueous solutions of both formic acid (HCOOH) and sodium hydroxide (NaOH) were used for the synthesis of UF resins. An aqueous solution of ammonium chloride (NH<sub>4</sub>Cl) was used as a hardener. The pMDI was Lupranate M20S from BASF, Germany, with an -NCO content of 31%. Sodium bisulfite (NaHSO<sub>3</sub>) was used as a blocking agent for the pMDI resin, acetone as solvent, and sodium dodecyl sulfate as surfactant. Meranti (*Shorea spp*) veneers were used for plywood fabrication.

### 2.2. Preparations of the hybrid resin

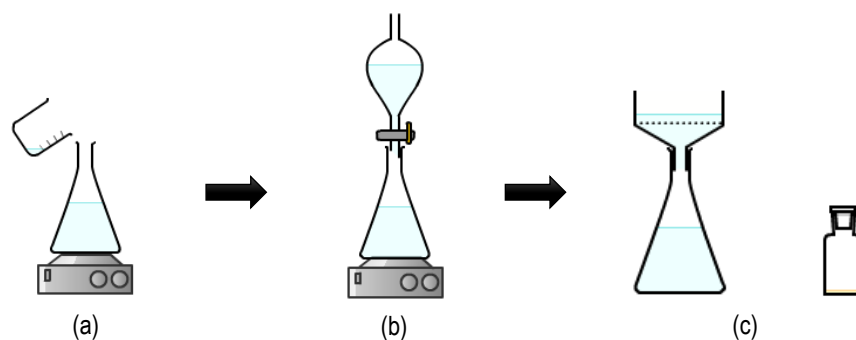
#### 2.2.1. Synthesis of the UF resin

A UF resin with a final mole ratio of 1.0 F/U was prepared by an alkaline-acid two-step reaction. First, approximately 500 g of formalin (37%) was placed in a reactor and stirred at 180 revolutions per minute (RPM). The mixture was adjusted to a pH of 7.8–8.0 using NaOH solution (20%) before the temperature reached 40 °C. Then, 187 g of urea was added into the reactor. The mixture was heated to 90 °C, and the temperature was kept stable at 90 °C for 1 h to maintain the methylation reaction. Afterward, the temperature was adjusted to 80 °C. When the temperature reached 83 °C, the pH was adjusted to 4.6 using formic acid solution (20%). The condensation reactions were conducted until a target viscosity of J-K (between 250-275 mPa·s) was reached, which was measured using a bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA). When the target viscosity was reached, the pH was increased again to the alkaline range, and again 187 g of urea was added to the reactor. After all of the urea was dissolved, the UF resin was cooled to room temperature, and the pH adjusted to 8.0.

### 2.2.2. Synthesis of B-pMDI resin

B-pMDI resins with four different HSO<sub>3</sub>⁻/NCO mole ratios (0.9, 1.2, 1.5, and 1.8) were prepared in the laboratory. A four-neck flask was carefully purged with nitrogen in order to remove air and to obtain a nitrogen atmosphere. Subsequently, an aqueous solution of NaHSO<sub>3</sub> (40 wt%) was mixed with acetone to obtain a 20 wt% aqueous NaHSO<sub>3</sub> solution. After stirring for 10 min at 400 RPM, the calculated amounts of pMDI (80% in acetone) were introduced dropwise into the solution under agitation to obtain the various HSO<sub>3</sub>⁻/NCO mole ratios. The blocking reaction was maintained at 25 °C for 1 h. Subsequently, the mixture was

filtered using vacuum filtration. Solid B-pMDI resin powder was obtained by vacuum drying at 50 °C for 24 h. **Fig. 1** illustrates the procedure for the preparation of B-pMDI.



**Fig. 1.** Procedure for preparing B-pMDI: (a) mixing  $\text{NaHSO}_3$  with acetone, (b) dropping pMDI into  $\text{NaHSO}_3$  solution, (c) filtration for B-pMDI resin powder preparation

### 2.2.3. Preparation of UF/B-pMDI resin

Hybrid UF/B-pMDI resins were prepared in the laboratory by adding B-pMDI with different  $\text{HSO}_3^-/\text{NCO}$  mole ratios into the UF resin. A certain amount of the UF resin (70 g) was prepared in a glass beaker with a volume of 200 mL. Furthermore, 1 and 3% of B-pMDI powder (based on the UF resin solid content) for each  $\text{HSO}_3^-/\text{NCO}$  mole ratio was added to obtain the various hybrid UF/B-pMDI resins. 5% of sodium dodecyl sulfate (based on the B-pMDI weight) was then added to the mixture as a surfactant. Subsequently, 10 % of wheat flour (based on the total resin weight) and 3% of  $\text{NH}_4\text{Cl}$  (20% wt) were introduced into the solution. Finally, the solution was agitated at 10,000 rpm using a homogenizer (Unidrive X1000D, CAT GmbH, Germany) until a homogenous solution was obtained.



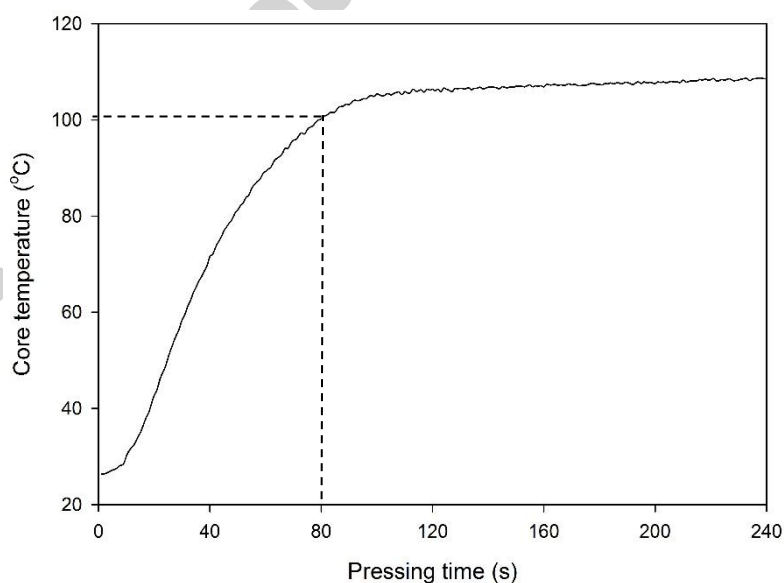
**Table 1.** Properties of hybrid UF/B-pMDI resins used in this study

Properties	B-pMDI addition level (wt %)*	HSO <sub>3</sub> /-NCO mole ratio				
		0	0.9	1.2	1.5	1.8
Non-volatile solids content (wt %)	1	56.5	56.8	57.3	57.8	57.9
	3	56.5	57.6	57.7	58.1	58.1
pH	1	7.8	7.8	7.9	8.0	8.0
	3	7.8	7.9	8.0	8.0	8.0

\*The addition level is based on the solids content of UF resin

### 2.3. Plywood manufacturing

Plywood with a size of 300 mm × 300 mm × 6 mm was fabricated using meranti (*Shorea spp.*) veneers and UF/B-pMDI resins. The amount of glue spread used was 170 g/m<sup>2</sup> for manufacturing 3-ply plywood. The plywood was cold-pressed for 1 h and then hot-pressed at 120 °C and 0.78 MPa for 240 s. The core temperature of the plywood was measured with a thermocouple placed in the core veneer during the hot-pressing. As expected, the core temperature of plywood reached 100 °C in 80 s during hot-pressing (Fig. 2).



**Fig. 2.** The core temperature profile of plywood bonded with UF/B-pMDI resin at the 3% addition of B-pMDI and the mole ratio of 1.8 as measured by a thermocouple during hot-pressing.

#### 2.4. Characterization of B-pMDI resin

Fourier transformation infrared (FTIR) spectra of all prepared B-pMDI resins and of pure pMDI were recorded using attenuated total reflection (ATR) FTIR spectroscopy (Alpha P, Bruker Alpha, Germany) in the range of  $400 \sim 4,000 \text{ cm}^{-1}$  at room temperature. Furthermore, the de-blocking temperature measurements were performed by pressurized differential scanning calorimetry (DSC) (Q10, TA Instrument, New Castle, DE, USA). Approximately 5 mg of resin samples were sealed in a hermetic pan and then heated from 30 to 200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

#### 2.5. Characterization of UF/B-pMDI resins

The viscosity of the UF/B-pMDI resins was determined using a cone-plate viscometer (DV-II<sup>+</sup>, Brookfield, Middleboro, MA, USA) with the No. 2 spindle at 60 RPM at 26 °C. The gel time of the neat and hybrid resins were measured at 100 °C using a gel time meter (Davis Inotek Instrument, Charlotte, NC) with two replications for UF/B-pMDI resins of different HSO<sub>3</sub>/-NCO mole ratios by adding 3 % NH<sub>4</sub>Cl as a hardener. Pressurized DSC within the temperature range 30 to 200 °C and a heating rate of 10 °C/min was used to determine the peak temperature ( $T_p$ ) and the heat of reaction ( $\Delta H$ ) as determined by the area under the exothermic curve for the UF/B-pMDI resins.

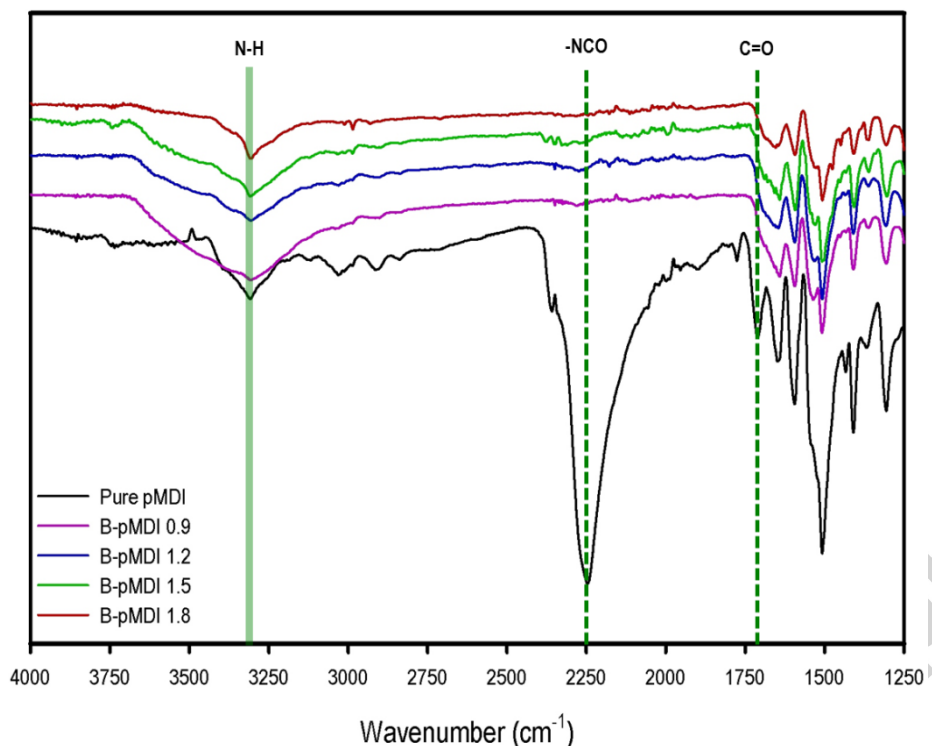
## 2.6. Evaluation of plywood properties

Plywood properties such as tensile shear strength in both dry and wet conditions, modulus of rupture (MOR), and formaldehyde emission were evaluated. Four and two specimens were prepared for the measuring the tensile shear strength (25 mm × 80 mm × 6 mm) and MOR (50 mm × 200 mm × 6 mm), respectively. The tensile shear strength and MOR were determined using a universal testing machine (H50KS, Hounsfield, Redhill, England) at a cross-head speed of 5 and 10 mm/min, respectively, according to Korean Standard (KS) F 3101 (2006) [22]. Statistical analysis of the data was conducted using SAS 9.4 software (SAS Institute Inc., Cary, NC, USA).

## 3. Results and discussion

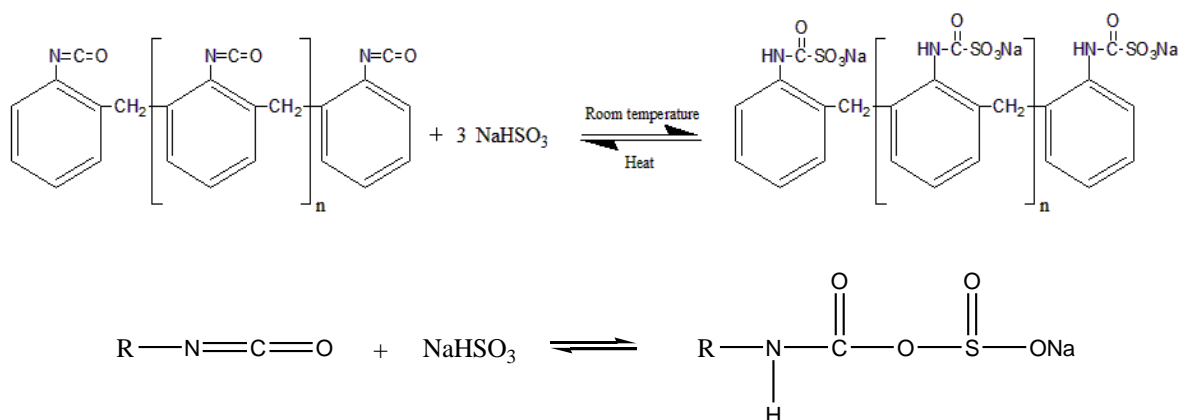
### 3.1. ATR FTIR analysis

In order to confirm the blocking reaction of pMDI with sodium bisulfite, FTIR spectroscopy was conducted for the B-pMDI product. The results are presented in **Fig. 3**. The NCO group has a characteristic absorption peak at 2,285–2,250  $\text{cm}^{-1}$ . The neat pMDI spectrum shows that the NCO peak appeared at 2,250  $\text{cm}^{-1}$ . After blocking with sodium bisulfite at different mole ratios, all the NCO peaks disappeared. This indicates that all the NCO groups had reacted with the bisulfonate group of the sodium bisulfite. An absorption peak between 1,770–1,700  $\text{cm}^{-1}$  was observed in the pure pMDI spectrum, which was assigned to the C=O group. Furthermore, strong absorption peaks between 3,401 and 3,195  $\text{cm}^{-1}$  (N-H stretching) were detected in the spectra of the various B-pMDI resins [23].



**Fig. 3.** ATR FTIR spectra of pure pMDI and the various B-pMDI at different  $\text{HSO}_3^-/\text{-NCO}$  mole ratios

During the blocking reaction, pMDI reacted with the active bisulfite to form a weak bond, as shown in **Fig. 4**. At an elevated temperature, e.g., during hot-pressing of the plywood, this blocking agent is de-blocked to liberate the NCO group of pMDI resin, which leads to further reactions, such as with water to form polyureas, or with the hydroxyl groups of wood components to form urethane bonds.



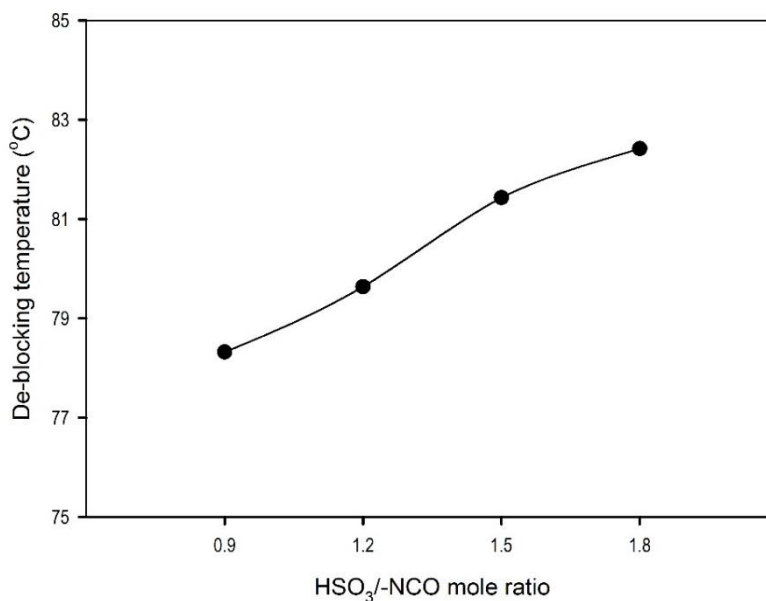
**Fig. 4.** Blocking and de-blocking mechanism of bisulfite B-pMDI [11]

In the process of blocking isocyanate groups with sodium bisulfite, there are competitive reactions between the isocyanate group and water or the solvents [8]. If the pMDI is not efficiently dispersed in an organic solvent, its reaction with water quickly produces carbon dioxide. This influences the extent to which blocking reactions will occur with the isocyanate group. We used acetone as a co-solvent for the blocking reaction, which eventually reduces the probability of the isocyanate group reacting with water molecules. This means that the use of a co-solvent is expected to cause the isocyanate group to react preferentially with sodium bisulfite rather than with water. Additionally, the dropwise method and the stirring speed employed has been shown to influence the reaction rate of the blocking of the isocyanate group with sodium bisulfate [13]. These workers reported that a stirring speed of 400 rpm resulted in a blocking rate of 96.8%. We can confirm that almost all the NCO groups of the pMDI resin were blocked with sodium bisulfate at all  $\text{HSO}_3^-/\text{-NCO}$  mole ratios.

### 3.2. Measurement of the de-blocking temperature of B-pMDI resins

The de-blocking temperatures of various B-pMDI resins were determined with DSC, using an endothermic phenomenon of the de-blocking reaction [11]. As shown in **Fig. 5**, the de-blocking temperature of B-pMDI resin ranged from 78.3 to 82.4 °C, depending on the HSO<sub>3</sub>/<sup>-</sup>NCO mole ratio. The de-blocking temperature increased linearly with the HSO<sub>3</sub>/<sup>-</sup>NCO mole ratio. This might be due to the fact that B-pMDI resins at higher mole ratio contain a greater amount of sodium sulfite than those of the low mole ratio B-pMDI resin. In other words, it is assumed that a greater amount of sodium bisulfate is expected to react with the -NCO group, which requires more energy to undertake the de-blocking process. Therefore, a higher temperature is needed to liberate the sodium bisulfate from the NCO groups in the B-pMDI resin.

The reported de-blocking temperature often depends on the method of analysis, heating rate of DSC, chemical structure of the blocking agent, chemical structure of the isocyanate monomer, and other variables [24, 25]. According to the DSC analysis, the B-pMDI had de-blocking temperatures ranging from 78 to 82 °C, depending on the mole ratio. The B-pMDI resins prepared in this study had low de-blocking temperatures compared with other blocked isocyanates. It was reported that the de-blocking temperature of B-pMDI resin with bisulfite was between 75 and 105 °C [11 -13]. Higher de-blocking temperatures have been reported for other blocked isocyanates [26]. Blocked isocyanates with methyl ethyl ketone oxime and caprolactam, had de-blocking temperatures ranging from 100 to 180 °C and 110 to 180 °C, respectively [26]. Based on its relatively low de-blocking temperature, the B-pMDI prepared with sodium bisulfite can be de-blocked below 100 °C in a curing system, such as in plywood manufacturing with a UF resin.

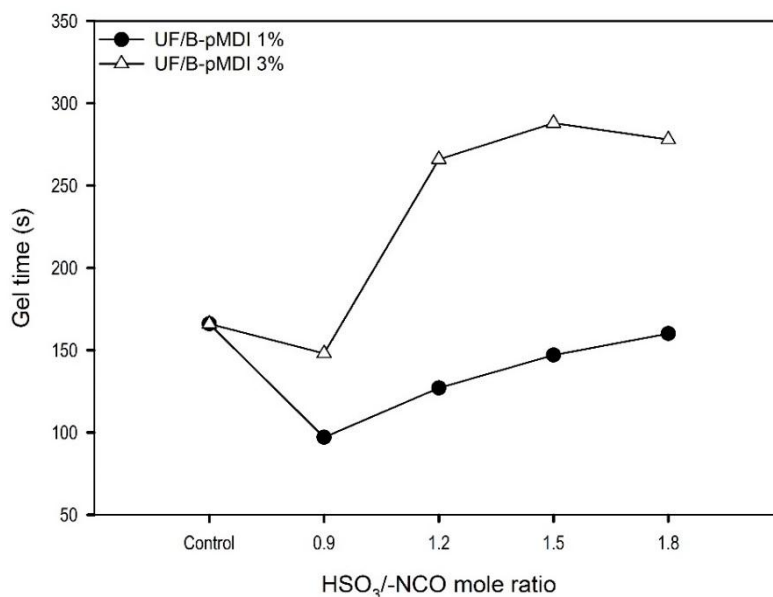


**Fig. 5.** De-blocking temperature of B-pMDI resins at different HSO<sub>3</sub>⁻/NCO mole ratios as measured by DSC

### 3.3. Properties of UF/B-pMDI resins

The gel time of hybrid UF/B-pMDI resins was determined to compare their activity, and the results obtained are displayed in **Fig. 6**. The gel time decreased from 166 (for the control) to 97 s with the addition of 1% B-pMDI resin at a mole ratio of 0.9. As the HSO<sub>3</sub>⁻/NCO mole ratio increased, the gel time gradually increased up to 160 s for the highest mole ratio. The addition of 3% B-pMDI resin to the UF resin also influenced the gel time. At a mole ratio of 0.9 the gel time decreased from 166 to 148 s. This is probably due to an increase in the reactivity of the hybrid resin at this mole ratio. The lowest amount of sodium bisulfate at this mole ratio probably increased the reactivity of the hybrid resin. But the gel time of B-pMDI resin with higher mole ratios increased up to 278 s, which had much greater values than that of the control. The results also showed that the gel time of the hybrid resin was strongly affected by the amount of added B-pMDI resin. That is, as the HSO<sub>3</sub>⁻/NCO mole

ratio increased, the pH of the hybrid resin increased slightly, reducing the reactivity of the hybrid resins. In addition, the greater amount of sodium bisulfate could also make the curing reaction slow and reduce the reactivity. Therefore, the curing rate of the UF/B-pMDI resin decreased with an increase in the mole ratio, yielding a longer gel time [27].

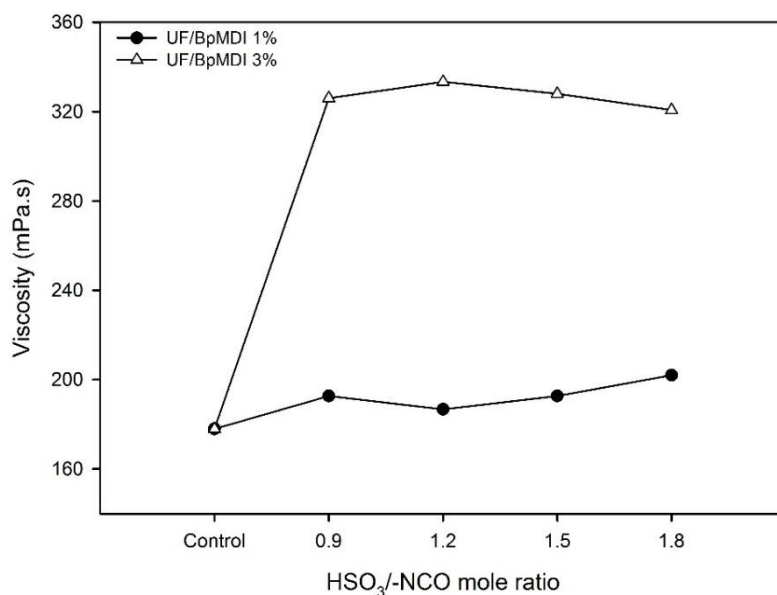


**Fig. 6.** Gel time of UF/B-pMDI resins at different B-pMDI addition levels and HSO<sub>3</sub>⁻/NCO mole ratios

**Fig. 7** shows the viscosity of the UF/B-pMDI resins. In general, the resin viscosity increased with the addition of B-pMDI. The viscosity increased from 178 to 202 mPa·s when 1 % B-pMDI resin at different mole ratios was added into the UF resins and increased from 178 to 320 mPa·s for the addition of 3 % B-pMDI resin at different mole ratios. As expected, the amount of B-pMDI resin added into the UF resin significantly influenced the viscosity of the hybrid resins. The addition of 3 % B-pMDI resin yielded a higher viscosity than for those



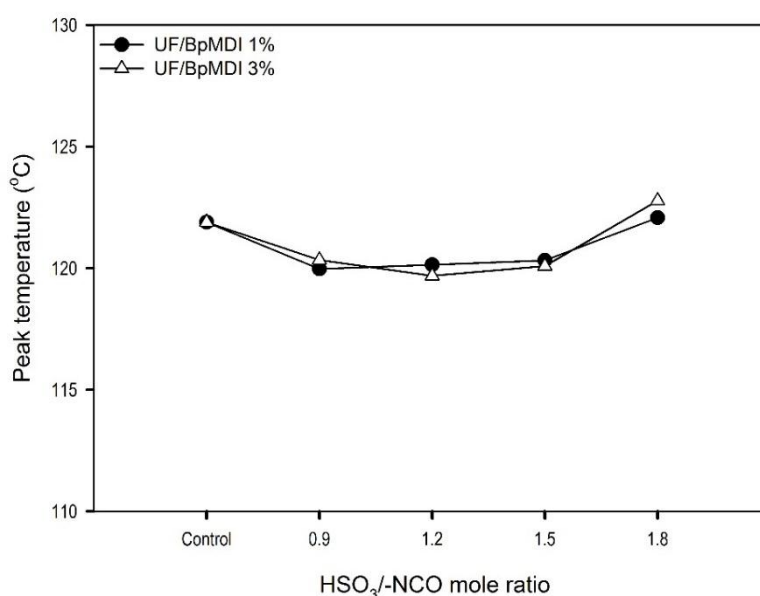
of 1 % B-pMDI, probably because the powdered B-pMDI resin was homogeneously dispersed in the UF resin, leading to an increase in viscosity. The influence of resin viscosity will be discussed further with regards the tensile shear strength of plywood bonded with UF/B-pMDI resins.



**Fig. 7.** Viscosity of UF/B-pMDI resins at different B-pMDI addition levels and HSO<sub>3</sub>/<sup>-</sup>NCO mole ratios

**Fig. 8** shows peak-temperature ( $T_p$ ) measurements for the UF/B-pMDI resins obtained using DSC, which were performed to understand the curing behavior of these modified resins. Neat UF resin as the control had a  $T_p$  of 121.9 °C.  $T_p$  values for all the UF/B-pMDI resins ranged from 119 to 123 °C, depending on the mole ratio of HSO<sub>3</sub>/<sup>-</sup>NCO. The addition of 1 and 3% B-pMDI resin into the UF resin decreased the  $T_p$  to 120 °C at all mole ratios except the highest, with  $T_p$  back to the level of the control. There is no clear influence of B-pMDI

resin content on the  $T_p$  of UF/B-pMDI resin. The results are partly consistent with the gel time measurements of the UF/B-pMDI resins (**Fig. 6**), which shows longer gel times as the mole ratio increases.



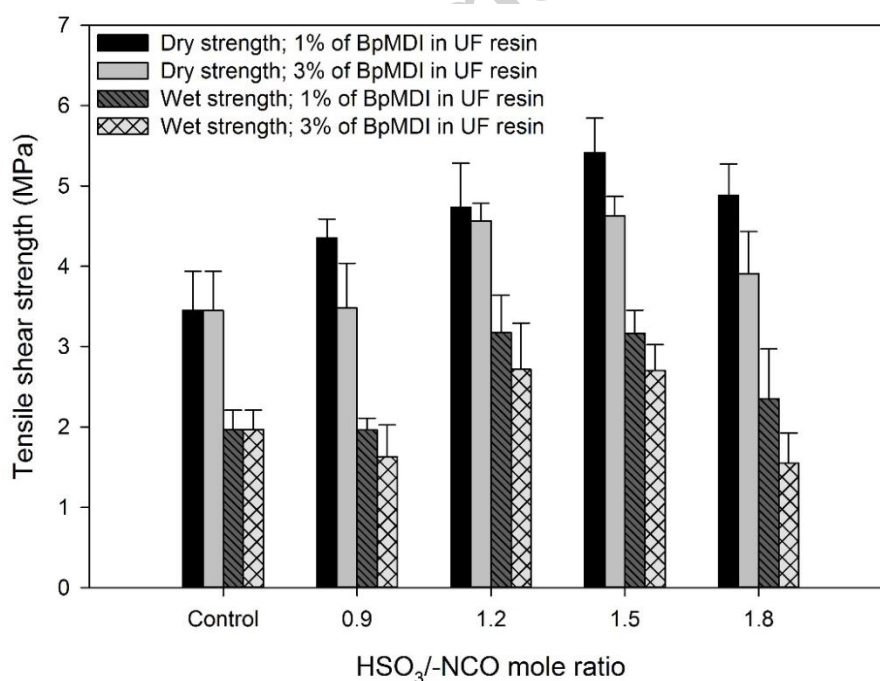
**Fig. 8.** Peak-temperature changes of UF/B-pMDI resins at different B-pMDI addition levels and HSO<sub>3</sub>/-NCO mole ratios

### 3.4. Plywood properties

#### 3.4.1. Adhesion performance of plywood

Dry and wet tensile shear strength of plywood bonded with UF/B-pMDI resin after the addition of 1 and 3 % B-pMDI resin were determined to compare the adhesion of hybrid resins, and the results are presented in **Fig. 9**. As expected, the B-pMDI resin had an obvious influence on the tensile shear strength of plywood with both dry and wet tensile shear strength values increasing as the mole ratio increased up to 1.5. Both dry and wet tensile shear strength values increased by 57 and 61%, respectively, compared with that of the

control. However, a further increase in the mole ratio up to 1.8 resulted in a decrease in both strengths, but the strength was still greater than that of the control. The highest tensile shear strength in the dry condition was 5.4 MPa for the UF/B-pMDI resin at a mole ratio of 1.5, with the lowest being 3.5 MPa for the neat UF resin. These high dry tensile shear strength values are attributed to the formation of various bonds between the de-blocked isocyanate group and the  $-CH_2OH$  groups of UF resins or those between the de-blocked isocyanate group and the hydroxyl group of wood. The formation of biuret, polyuret, and polyurea bonds between the  $-NCO$  group and the  $-CH_2OH$  groups of UF resins has been reported by DSC and NMR [5, 6, 21]. However, only limited formation of urethane bonds between the NCO groups and hydroxyl groups in wood has been reported, especially when huge excesses of pMDI were used [7, 27]. Statistical analysis also revealed that the dry tensile shear strength of plywood at a mole ratio of 1.5 was significantly different (Table 2).



**Fig. 9.** Dry and wet tensile shear strength of plywood bonded with UF/B-pMDI resin at 1 and 3% B-pMDI addition as a function of HSO<sub>3</sub>/-NCO mole ratio

A similar trend also occurred for the wet tensile shear strength of plywood. The highest value observed was 3.2 MPa for the UF/B-pMDI resin at a mole ratio of 1.5, with the lowest being 2.0 MPa for the neat UF resin. This might indicate an improvement in the water resistance of the plywood due to the incorporation of the B-pMDI resin into the UF resin. With an increase in the HSO<sub>3</sub>/-NCO mole ratio, the amount of -NCO groups decreased and the amount of sodium bisulfite increased. This probably resulted in the blocking reaction reaching an optimum level at a mole ratio of 1.5. Thus, the number of -NCO groups released after the de-blocking reaction was also at an optimum for reacting with CH<sub>2</sub>OH groups in the UF resins or with hydroxyl groups in the wood. Compared with dry tensile shear strength, the wet tensile shear strength of plywood decreased about 33% and 55% at the various mole ratios. The results of dry and wet tensile shear strengths of plywood bonded with the UF/B-pMDI resin with the addition of 3% B-pMDI resin followed the same trend as those for the addition of 1% B-pMDI. Both dry and wet tensile shear strength values increased with an increase in mole ratio up to 1.5. A further increase of mole ratio to 1.8 decreased the wet tensile shear strength. Compared with the control, the tensile shear strength was improved by 34 and 37% for dry and wet strength, respectively, at a mole ratio of 1.5. The highest dry tensile shear strength (4.6 MPa) was found for the UF/B-pMDI resin at a mole ratio of 1.5, while the lowest (3.5 MPa) was found for the control UF resin. However, the highest wet tensile shear strength (2.7 MPa) was for the UF/B-pMDI resin with a mole ratio of 1.5, while the lowest strength (1.5 MPa) was found for the UF/B-pMDI resin at a mole ratio of 1.8.

However, wet tensile shear strengths of plywood made from neat UF resin and UF/B-pMDI resin at a mole ratio of 0.9 and 1.8 were not significantly different from each other (Table 2). The results showed that the addition of 1% B-pMDI resin into the UF resin yielded a better adhesion performance than that of the 3% B-pMDI resin. As already explained, the addition of B-pMDI into the UF resin resulted in a higher viscosity. The addition of 3% B-pMDI resin yielded a higher viscosity for the UF/B-pMDI resin than that for the addition of 1% B-pMDI resin. In addition, many other factors such as chemical bond formation, resin reactivity, or resin penetration into the wood may also have affected this result.

**Table 2.** Result of Tukey multiple comparison test for plywood properties

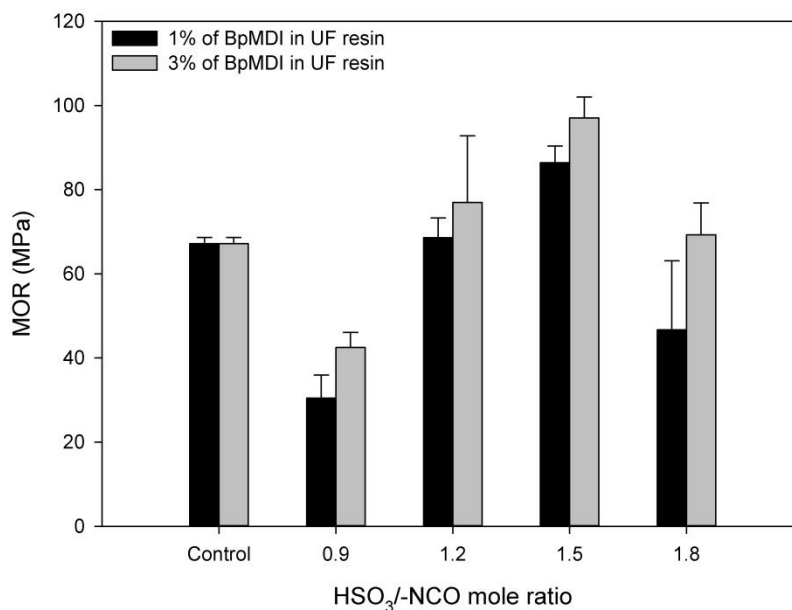
Properties	B-pMDI addition level (wt %)	HSO <sub>3</sub> /-NCO mole ratio				
		Control	0.9	1.2	1.5	1.8
Dry tensile shear strength	1	D*	B,C	B	A	B
	3	D	D	B	B	C,D
Wet tensile shear strength	1	C,D	C,D	A	A	B,C
	3	C,D	D	A,B	A,B	D
MOR	1	A,B	C	A,B	A	B,C
	3	A,B	C	A	A	A,B
Formaldehyde emission	1	A	A	B	B	F
	3	A	C	C,D	D,E	E

\*The same letters are not significantly different each other at a  $p$  value of 0.05.

### 3.4.2. Flexural properties of plywood

Flexural tests were performed to investigate the effects of the UF/B-pMDI resin on the mechanical properties of plywood according to the standard procedure [22]. **Fig. 10** presents the MOR of plywood bonded with UF/B-pMDI resins at different HSO<sub>3</sub>/-NCO mole ratios. As shown, in comparison to the UF resin control, the addition of both 1% and 3% B-pMDI at

a  $\text{HSO}_3^-/\text{NCO}$  mole ratio of 0.9 results in a reduction in MOR. However, on increasing mole ratio, MOR increased to a maximum at a mole ratio of 1.5, regardless of the addition level of B-pMDI resin. Statistical analysis also revealed that the MOR of plywood at a mole ratio of 1.5 was significantly different, regardless of the addition level of B-pMDI resin (Table 2). As shown in Fig. 10, the highest MOR values were 86.4 and 97 MPa for 1 and 3 % addition of the B-pMDI resin, respectively, at a mole ratio of 1.5, while the lowest MOR values were 30.4 and 42.4 MPa for 1 and 3% addition of the B-pMDI resin, respectively, at a mole ratio of 0.9. The MOR of plywood improved by 29 and 44% compared with that of the control sample with the addition of 1 and 3% B-pMDI, respectively. However, the application of UF/B-pMDI resin at a mole ratio of 0.9 reduced the MOR to 55 and 37%, respectively, compared with the UF resin control, regardless of the B-pMDI resin addition level. This was probably because the UF/B-pMDI resin at a mole ratio of 0.9 was more reactive than the control UF resin, which made the resin more viscous. In general, a high-viscosity resin results in poor resin penetration into wood tissue, which contributes to weak adhesion in the bond-line. The plywood MOR with the addition of 3% B-pMDI resin was slightly greater than that with that of the 1 % B-pMDI addition. This was probably because the addition of 3 % B-pMDI resin yielded a lower  $T_p$  than did the 1 % B-pMDI addition. This could probably help the resin achieve the cured state. In addition, with an increase in the  $\text{HSO}_3^-/\text{NCO}$  mole ratio, the number of -NCO groups decreased and the amount of bisulfite increased. This probably resulted in the blocking reaction reaching an optimum state at a mole ratio of 1.5, regardless of the amount of B-pMDI resin added. Therefore, the MOR of plywood increased to its maximum at a mole ratio of 1.5.

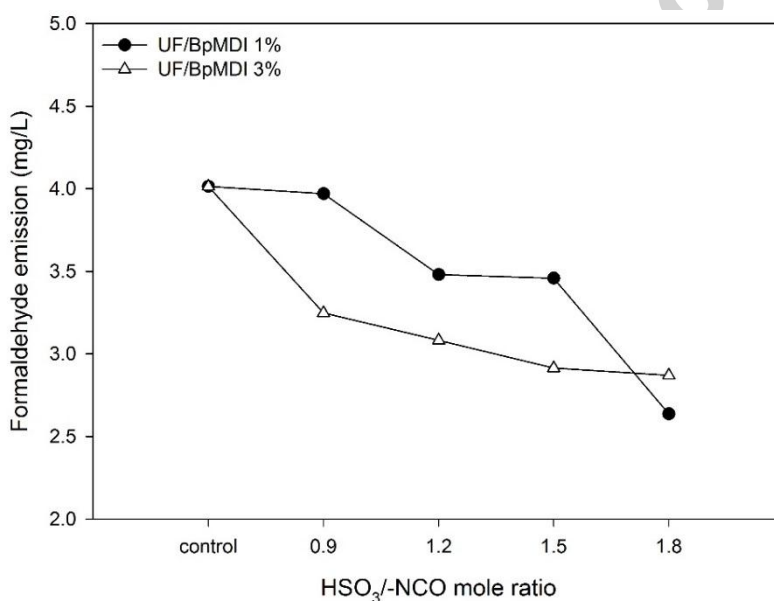


**Fig. 10.** Bending strength of plywood bonded with UF/B-pMDI resin at 1 and 3 % B-pMDI addition as a function of HSO<sub>3</sub>⁻/NCO mole ratio.

### 3.4.3. Formaldehyde emission

**Fig. 11** shows the formaldehyde emission of plywood bonded with UF/B-pMDI resins with the addition of 1 and 3 % B-pMDI resin at different HSO<sub>3</sub>⁻/NCO mole ratios. The plywood bonded with neat UF resin resulted in a formaldehyde emission of 4.0 mg/L. The results show that the addition of B-pMDI resin into the UF resin greatly decreased the formaldehyde emission from the plywood. The addition of 1 and 3 % B-pMDI resin at a mole ratio of 1.8 significantly reduced the emission, by 34 and 32 %, respectively. The formaldehyde emission from plywood bonded with UF/B-pMDI resins with the addition of 1 % B-pMDI resin was higher than that for the addition of 3 % B-pMDI resin, except the highest mole ratio. Statistical analysis also showed that the formaldehyde emission of plywood bonded with UF/B-pMDI resins with the addition of 1 % B-pMDI resin were significantly

different compared to the addition of 3% B-pMDI resin (Table 2). This was probably due to the lower concentration of -NCO groups in the UF/B-pMDI resin with 1% B-pMDI resin compared with the case of 3% B-pMDI. The -NCO groups probably could react with the free formaldehyde (HCHO) and formed HNCO [29]. Thus, the UF/B-pMDI resins with the addition of 3% B-pMDI resin had more opportunity to reduce the formaldehyde emission. In addition, the amount of -NCO group decreased and the amount of bisulfite increased with an increase in the  $\text{HSO}_3^-/\text{-NCO}$  mole ratio. Therefore, the amount of bisulfite at the mole ratio of 1.8 was almost double from the amount of -NCO group. Probably this made the excess of bisulfite react with free formaldehyde which eventually reduced the emission.



**Fig. 11.** Formaldehyde emission of plywood bonded with UF/B-pMDI resin at 1 and 3% B-pMDI resin addition as a function of  $\text{HSO}_3^-/\text{-NCO}$  mole ratio.



#### 4. Conclusions

Blocking of the isocyanate groups of pMDI by sodium bisulfite in order to obtain water-dispersible B-pMDI resin in powder form was confirmed via ATR-FTIR spectra. It showed that the NCO peak at  $2250\text{ cm}^{-1}$  disappeared after the blocking reaction. DSC analysis of the B-pMDI resin showed that all de-blocking temperatures of B-pMDI resin were in the range of from 78 to 82 °C as the  $\text{HSO}_3^-/\text{NCO}$  mole ratios increased from 0.9 to 1.8. All these de-blocking temperatures were below 100 °C which was the core temperature of plywood during hot-pressing. The properties of the hybrid UF/B-pMDI resins depended significantly on the amount of added B-pMDI resin. Better adhesion strength was obtained for plywood bonded with UF/B-pMDI resins compared with those bonded with neat UF resins. All tensile shear strengths of plywood bonded with the hybrid resins were greater with the addition of 1% B-pMDI than with the addition of 3% B-pMDI resin. Based on the Tukey multiple comparison analysis, all wet tensile shear strengths of plywood bonded with hybrid UF/B-pMDI resins were greater than those of neat UF resins. The statistical analysis also showed that the wet tensile shear strength of plywood made from neat UF resin and UF/B-pMDI resins at mole ratios of 0.9 and 1.8 were not significantly different from each other. Regarding the  $\text{HSO}_3^-/\text{NCO}$  mole ratio, the addition of B-pMDI resin at a mole ratio of 1.5 resulted in better performance for plywood, regardless of the amount of added B-pMDI resins. Probably this made the blocking reaction reach an optimum at the mole ratio of 1.5. The amount of  $-\text{NCO}$  groups above the de-blocking temperature did reach an optimum for the reaction either with  $-\text{CH}_2\text{OH}$  groups of the UF resins or with the hydroxyl groups of wood. The formaldehyde emission from plywood bonded with UF/B-pMDI resins was significantly decreased by up to 34% upon the addition of B-pMDI resin at a mole ratio of 1.8, regardless of the amount of

added B-pMDI resins. The results obtained from this study suggest that the modification of UF resins with B-pMDI resin is a way of improving the water resistance and formaldehyde emission characteristics of UF resins for wood-based composites.

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