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Microencapsulation of polymeric isocyanate for the modification of urea-formaldehyde resins

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ABSTRACT

This study was conducted to prepare the microcapsules of polymeric 4-4 diphenyl methane diisocyanate (MpMDI) by interfacial polymerization using two different surfactants (Tween 40 and Gum Arabic) for the modification of urea-formaldehyde (UF) resins. MpMDI obtained by Tween 40 (TW-MpMDI) were spherical, smooth, and small diameter, while those prepared by Gum Arabic (GA-MpMDI) were irregular, rough surface, and larger diameter. Attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectra of two types of MpMDIs confirmed the successful microencapsulation of pMDI by detecting the isocyanate (N═C═O) groups after rupturing the shell of MpMDIs. As the MpMDI content in UF resins increased, the non-volatile solids content, pH, gelation time, viscosity, and exothermic peak temperature of UF/MpMDI adhesives slightly increased. Plywood bonded with UF/MpMDI adhesives had 15% higher tensile shear strength (TSS) and 30% higher modulus of rupture (MOR) than those of the plywood bonded with neat UF resins owing to the formation of urethane (HN-(C═O)–O-R) bonds. In particular, plywood bonded with UF/TW-MpMDI had higher TSS and MOR values than those bonded with UF/GA-MpMDI adhesive. Regardless of the surfactant types, the formaldehyde emission decreased about 54% with 5% MpMDI addition into UF resins. These results and statistical analysis revealed that 1% TW-MpMDI addition into UF resins provided a proper balance between good adhesion and low formaldehyde emission for plywood.

1. Introduction

As the main adhesive in the manufacture of wood-based composites, urea-formaldehyde (UF) resins have a critical disadvantage, namely formaldehyde emission (FE) [1]. To reduce the emission, several modifications such as lowering the formaldehyde/urea mole ratio [2], adding different amines [3], incorporating organic and inorganic nanomaterials [4,5], and modification with biopolymer [6] have been done. However, the modifications do not improve the adhesion performance of UF resins owing to a decrease in UF resins reactivity. A way to improve adhesion performance and reduce the FE is to mix UF resins with isocyanates [7].

Isocyanates have become one of the major chemicals in the world owing to their versatility since found in 1848 [8,9]. Toluene diisocyanate and methylene diphenyl isocyanate are the mostly used isocyanates. However, the isocyanates are very sensitive to moisture and have a short storage life, which limits their uses [10]. To overcome these disadvantages, a method called blocking isocyanates has been developed [11]. A blocked isocyanate is formed via a reaction between an –NCO group and a blocking agent which has an active hydrogen atom to block the –NCO [11-13]. However, the application of blocked isocyanates is limited because of high de-blocking temperature to release the –NCO groups. Another way of blocking the isocyanates is to cover the –NCO groups through microencapsulation.

Microcapsules are micro containers with an active chemical [14], and can be prepared through chemical and physical microencapsulation [15]. Surfactants are often used to increase the yield of microencapsulation by decreasing the interfacial tension [16,17]. The microencapsulation of isocyanate is usually done by means of interfacial polymerization, and the isocyanate microcapsules are widely used as self-healing materials in polymer composites [14,18]. When the microcapsules rupture, it releases the active –NCO groups and reacts with the main polymer. Therefore, the isocyanate microcapsules are good options of using as wood adhesive or a modifier, owing to the similarity of protecting and releasing the –NCO groups as the blocked isocyanates.

Described in here is the preparation of isocyanate microcapsules and

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the use of microcapsules for the modification of UF resins. Polymeric 4,4 methylene diphenyl isocyanate (pMDI) was selected as the core material and 1,4 butanediol was used as the chain extender to form the microcapsules shell. Characteristics of microcapsule pMDI (MpMDI) were evaluated using light microscopy (LM), field-emission scanning electron microscopy (FE-SEM), and attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectroscopy. Basic properties, thermal properties, and chemical properties of UF/MpMDI adhesives were investigated using several techniques. The adhesion performance and formaldehyde emission of UF/MpMDI adhesives in plywood were also evaluated. For the first time, this paper reports the incorporation of MpMDI into UF resins as a part of improving the adhesion performance and reducing formaldehyde emission of UF resins-bonded plywood.

2. Experimental procedure

2.1. Materials

Technical-grade urea granules (99 wt%), formalin (37 wt%), formic acid (20 wt%) and sodium hydroxide (20 wt%) were used for the synthesis of UF resins. An aqueous solution of ammonium chloride (20 wt%) was used as a catalyst. The pMDI was Lupranate M20S (BASF, Mannheim, Germany) with 31% of –NCO content. Gum Arabic, Tween 40, and 1,4 butanediol were used for microencapsulation of pMDI. Radiata pine (*Pinus radiata* D. Don) veneers were used to fabricate the plywood.

2.2. Preparations of UF/MpMDI adhesives

2.2.1. Microencapsulation of pMDI

Two MpMDIs were prepared using interfacial polymerization with two different surfactants such as Gum Arabic (GA) and Tween 40 (TW). GA and TW were selected as emulsifiers in the microencapsulation of pMDI because of their ability to reduce surface tension and to produce small diameter of microcapsules [19,20]. Approximately 5 mL of pMDI was mixed with 30 g GA solution (3 wt%) and stirred for 10 min. Around 50 g of 1,4 butanediol was dropped into the mixture at a dropping rate of 1.0 mL/min. The microencapsulation was completed after stirring at different agitation rates of 300, 400, 500, and 600 RPM for 30 min at 60 °C and at different temperatures of 25, 40, 60, and 80 °C under 400 RPM of agitation rate. Subsequently, the mixture was filtered using vacuum filtration and then air dried for 24-h to obtain the GA-MpMDI. For TW-MpMDI, 5 mL of pMDI was mixed and stirred with 0.0625 g of Tween 40 and 50 g of 1.4 butanediol was dropped into the mixture. TW-MpMDI was also obtained after vacuum filtration and air drying.

2.2.2. Synthesis of UF resins

Liquid UF resins with a final F/U mole ratio of 1.0 was prepared according to the literature [21,22]. Briefly, approximately 500 g of formalin was placed in a reactor and the pH was adjusted to 8.0, then 187 g of urea was added into the reactor. The mixture was heated to 90 °C and kept stable for 1 h for the addition reaction. The temperature was then adjusted to 80 °C and the pH was adjusted to 4.6 for the condensation reaction. After reaching the target viscosity, around 187 g of urea was added to adjust the final F/U mole ratio. After all of the urea was dissolved, UF resins were cooled to room temperature, and the pH was adjusted to 8.0. The resins were kept in room temperature for 24 h prior to analysis.

2.2.3. Preparation of UF/MpMDI adhesives

UF/MpMDI adhesives were prepared by mixing UF resins with TW- and GA-MpMDI that had been microencapsulted at 25 °C and 400 RPM. Around 70 g UF resins was mixed with 1, 3, and 5% of MpMDI (based on the non-volatile solids content of UF resins) were added to obtain the UF/MpMDI adhesives. Furthermore, 10% wheat flour (based on the total weight of resins) and 3% ammonium chloride (based on the non-volatile solids content of UF resins) were mixed into the adhesives. Finally, the adhesives were agitated at 10,000 RPM using a homogenizer (Unidrive X1000D, CAT GmbH, Tübingen, Germany) until a homogenous solution was obtained.

2.3. Fabrication of plywood

Three-ply plywood panels (300 mm × 300 mm × 6 mm) were manufactured using Radiata pine (*Pinus radiata* D. Don) veneers and UF/MpMDI adhesives. The amount of glue spread was 170 g/m^2. The plywood was cold-pressed at 0.8 MPa for 20 min and then hot-pressed at 120 °C and 0.8 MPa for 4 min. Plywood panels were conditioned at room temperature for 2 days prior to analysis.

2.4. Characterization of MpMDI

Functional groups of each MpMDI before and after rupturing the shell were recorded using ATR–FTIR spectroscopy (Bruker Alpha, Ettlingen, Germany) in the range of 400–4000 cm^{-1} at room temperature. In addition, pure pMDI was also used as the control. All spectra were normalized using the min-max normalization method. A certain amount of MpMDI from each experimental unit was placed on the microscope cover glass and then vacuum dried at 7.4 Psi and 50 °C for 24 h. Both LM (BX 50F4, Olympus, Tokyo, Japan) and FE-SEM (SU 8220, Hitachi, Tokyo, Japan) were employed to confirm the formation and morphology of microcapsules. For FE-SEM, the MpMDI sample was then coated with platinum using ion sputtering E−1030 for 10 min Prior to analysis. Microcapsule diameters were measured using image analyzer (IMT *i*-solution Inc., British Columbia, Canada).

2.5. Properties of UF/MpMDI adhesives

The properties of UF/MpMDI adhesives were determined according to the published methods [23,24]. The viscosity of UF/MpMDI adhesives was measured using a cone-plate viscometer (DV-II^{+}, Brookfield, Massachusetts, United States) with the No. 2 spindle at 60 RPM and 25 °C. The gelation time of neat UF resins and UF/MpMDI adhesives were measured at 100 °C using a gel time meter (Davis Inotek Instrument, North Carolina, United States). Non-volatile solids contents of neat UF resins and UF/MpMDI adhesives were determined by drying 2 g of the sample in an oven at 105 °C for 3 h and dividing the oven-dried weight by the initial weight. Each experiment was repeated three times. The peak temperature (T_p) of UF/MpMDI adhesives mixed with 3% ammonium chloride (based on the solids content of resins) was scanned using DSC (Discovery 25, TA Instrument, New Castle, United States) from 30 °C to 200 °C with a heating rate of 10 °C/min under 50 mL/min of nitrogen gas. The spectra of cured UF/GA-MpMDI and cured UF/TW-MpMDI adhesives were also recorded using ATR-FTIR spectroscopy in the range of 400–4000 cm^{-1} at room temperature to detect any changes in the UF/MpMDI adhesives chemistry.

2.6. Evaluation of plywood properties

Plywood properties such as tensile shear strength (TSS), modulus of rupture (MOR) and formaldehyde emission (FE) were evaluated according to the procedure of a Korean standard [25]. Six and three specimens were prepared for the measuring the TSS and MOR, respectively. Both TSS and MOR were determined using a universal testing machine (H50KS, Hounsfield, Redhill, England) with a cross-head speed of 2 and 10 mm/min, respectively. FE values of plywood were measured using a 24 h desiccator method and UV–visible spectrophotometry (Optizen 3220 UV, Mecasys, Daejon, Korea) at a wavelength of 412 nm. Statistical analysis was conducted to compare the plywood properties using a multivariate analysis and Duncan multiple range test at $\alpha = 0.05$ using SPPS 17 software (SPSS Inc., Chicago, United States).

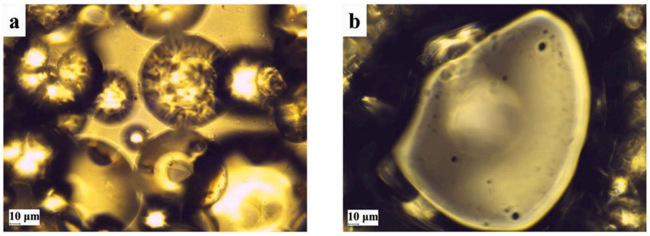

Fig. 1. Typical LM images (x10 magnification) of (a) TW-MpMDI and (b) GA-MpMDI prepared at 25 °C under 400 RPM.

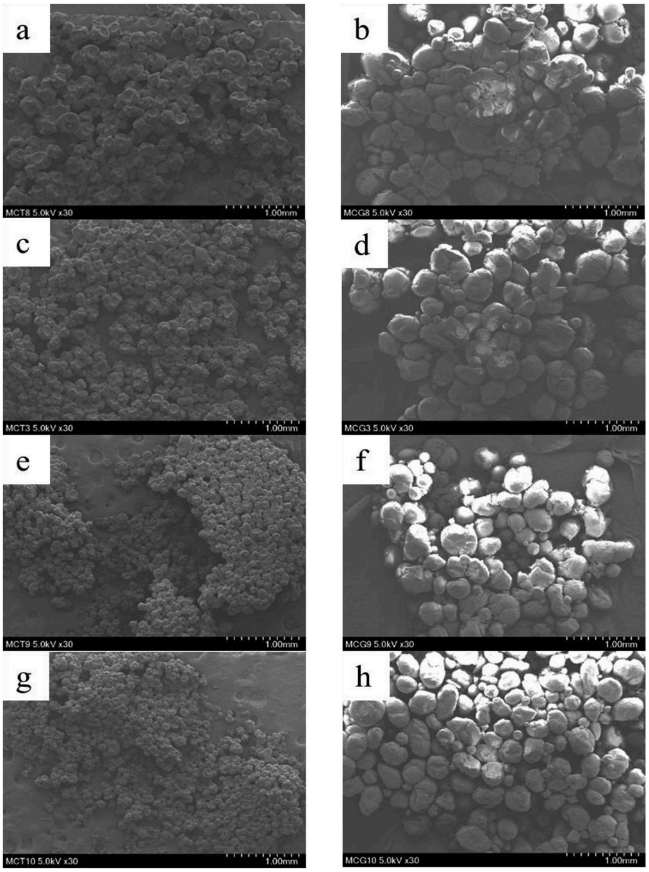

Fig. 2. Typical FE-SEM micrographs (x30 magnification) of MpMDI prepared at 25 °C and at different agitation rates and surfactants. (a) Tween 40 at 300 RPM, (b) Gum Arabic at 300 RPM, (c) Tween 40 at 400 RPM, (d) Gum Arabic at 400 RPM, (e) Tween 40 at 500 RPM, (f) Gum Arabic at 500 RPM, (g) Tween 40 at 600 RPM, (h) Gum Arabic at 600 RPM.

3. Results and discussion

3.1. *Characteristics of microcapsules pMDI*

Microencapsulation is a technology of making small droplets of liquid or solid encapsulated into individual shells [26]. In order to find a proper reaction condition, four agitation rates and four reaction temperatures were employed to prepare the MpMDIs. In this work, the LM and FE-SEM analysis were applied to ensure the formation of MpMDI. The LM analysis showed that TW-MpMDI were spherical while GA-MpMDI were irregular form (Fig. 1). FE-SEM micrographs also confirmed the results observed by LM (Fig. 2). The surface of TW-MpMDI was smooth and had many dents while the GA-MpMDI had quite rough surface that were possibly resulted from uneven reaction kinetic of the microencapsulation [27]. The size of TW-MpMDI became smaller as the agitation rate increased, while the opposite trend happened for GA-MpMDI. Similar to MpMDI prepared at different agitation rates, the surface of TW-MpMDI prepared at different temperatures was smooth while the GA-MpMDI was rough and irregular. Compared to agitation rate, the reaction temperature showed greater impact to the capsule diameter than the agitation rate. The large droplets are probably broken by shear forces and interfacial tension that has been created from higher agitation rate while higher temperature may swell the microcapsules [18]. This is consistent with the results presented in Fig. 3.

The average diameter of MpMDIs at different agitation rates and reaction temperatures is presented in Fig. 3. The average diameter of GA-MpMDI increased while the TW-MpMDI decreased as the agitation rate increased. By contrast, the average diameter of both MpMDI increased as the reaction temperature increased. In overall, the average diameter of TW-MpMDI was smaller than those of GA-MpMDI. The use of Tween 40 surfactant resulted in oil-in-oil interfacial polymerization while Gum Arabic was water-in-oil. The former probably produced more compatible environment for microencapsulation [28], and thus resulted in smaller average diameter as the agitation rate increased [18]. The agitation rate of 400 RPM and reaction temperature of 25 °C was selected as a proper microencapsulation condition because this condition resulted in medium average diameter of MpMDI, which would provide a good dispersion in UF resins.

In order to confirm the presence of pMDI in the microcapsules, the MpMDIs were scanned before and after their rupture. ATR-FTIR spectra of MpMDIs prepared by two types of surfactant are displayed in Fig. 4a and b. Before the rupture of MpMDIs, ATR-FTIR scanned only on the shell of MpMDIs, but the core of MpMDIs was observed after its rupture. Before its rupture, the –NCO groups at 2250 cm^{-1} and C═C aromatic of pMDI at 1530 cm^{-1} were not detected in MpMDIs because it was covered by the shell consisting of urethane bonds (1650 cm^{-1}). The shell of MpMDIs was formed via the reaction between the –OH groups of 1,4 butanediol and –NCO groups of pMDI [29]. The –NCO groups appears at 1710 cm^{-1} after rupturing the MpMDI shell. These spectra confirmed

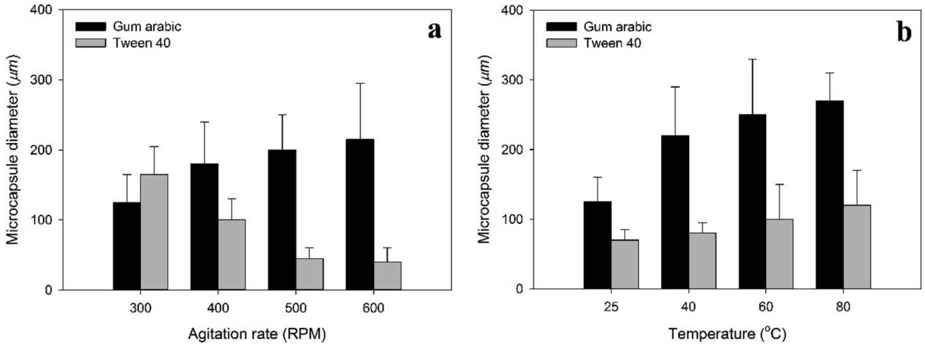

Fig. 3. Average diameter of MpMDI with two different surfactants as a function of (a) agitation rate and (b) temperature.

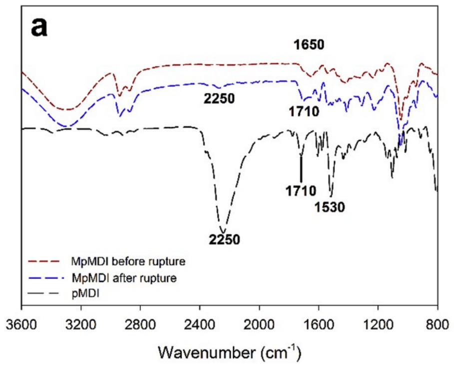

Fig. 4. Typical ATR-FTIR spectra of (a) GA-MpMDI and (b) TW-MpMDI prepared at 25 °C and 400 RPM of agitation rate.

Table 1
Properties of UF/MpMDI adhesives as a function MpMDI content and surfactant type.

Properties	GA-MpMDI content (wt %)				TW-MpMDI content (wt %)			
	0	1	3	5	0	1	3	5
Non-volatile solids content (%)	60.8 (0.32)[a]	61.3 (0.23)	61.7 (0.24)	61.9 (0.34)	60.8 (0.32)	61.9 (0.34)	63.2 (0.46)	63.5 (0.22)
Viscosity (mPa·s)	287 (6.48)	304 (3.91)	315 (8.68)	322 (6.98)	287 (6.48)	308 (8.91)	321 (4.95)	326 (6.08)
Gelation time (s)	181 (2.88)	191 (2.89)	200 (4.04)	208 (3.21)	181 (2.88)	190 (5.00)	199 (5.03)	210 (2.00)
pH	7.95 (0.05)	8.02 (0.03)	8.08 (0.03)	8.11 (0.03)	7.95 (0.05)	7.97 (0.02)	8.02 (0.02)	8.06 (0.04)

[a] Values in parentheses are the standard deviation.

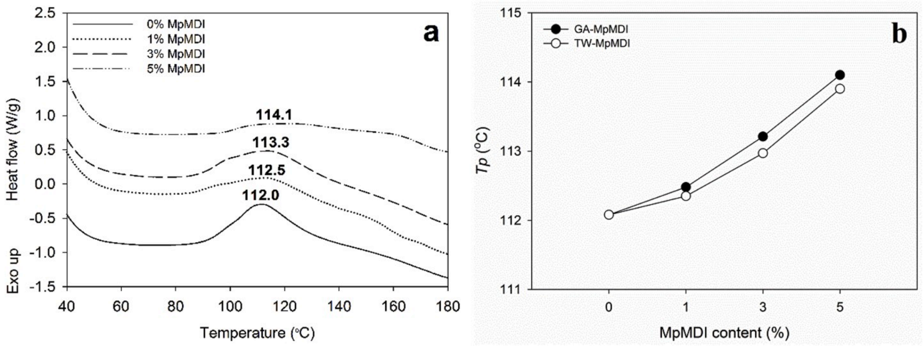

Fig. 5. (a) Typical DSC thermograms of UF/GA-MpMDI at different MpMDI contents scanned at 10 °C/min and (b) T_p values of UF resins as a function of MpMDI content and type of surfactant.

that the pMDI had been successfully encapsulated in this study. However, it should be noticed that the intensity of –NCO groups of MpMDIs after the shell rupturing was much lower than the pure pMDI, indicating that most of –NCO groups had been reacted with 1,4 butanediol to form the urethane shell.

3.2. Basic properties of UF/MpMDI adhesives

Since basic properties such as non-volatile solids content, pH, gelation time, and viscosity are affecting the performance of the adhesives in wood-based panels, properties of UF/MpMDI adhesives at different MpMDI contents and surfactant types are presented in Table 1. In general, non-volatile solids content, pH, gelation time, and viscosity of UF/MpMDI adhesives increased as a function of MpMDI content. UF/TW-MpMDI had higher solids content and viscosity than those of UF/GA-MpMDI adhesives while UF/GA-MpMDI had slightly higher pH and quite similar gelation time to those of the UF/TW-MpMDI. The presence of MpMDI in UF resins did not change the resins properties significantly. This is probably due to that the MpMDI is still in the microcapsule form without exposing the –NCO groups [29]. Cracking of MpMDI could release the –NCO into UF resins and alter its properties due to the reaction between –NCO groups and hydroxymethyl groups of UF resins.

3.3. Thermal and chemical properties of UF/MpMDI adhesives

DSC analysis showed the neat UF resins had a T_p around 112 °C (Fig. 5). Incorporating MpMDI into UF resins slightly increased the T_p to 114 °C. Regardless of the surfactant type, the MpMDI content increase from 1 to 5% moved the T_p to higher temperature. This could be due to that the amount of UF resins was reduced as the MpMDI content increased, thus resulting in higher T_p of UF/MpMDI adhesives and broader exothermic peak. In addition, it was likely no reaction between hydroxymethyl groups of UF resins and the –NCO groups inside the MpMDI to form urethane bonds [29], because no cracking was occurred in the UF/MpMDI adhesives during DSC scan. As shown in Fig. 4a, the –NCO groups are not detected before the rupturing of MpMDI shell.

Additional work was done to study chemical reactions of cured UF/MpMDI adhesives using ATR-FTIR spectroscopy. Regardless of the surfactant types, the addition of MpMDI into UF resins increased the intensity of N–H at 3329 cm^{-1} and C–H at 2940 cm^{-1} and 2860 cm^{-1} (Fig. 6a and b). This was obviously believed to be originated from the MpMDI that consisted of N–H and C–H of pMDI and 1,4 butanediol,

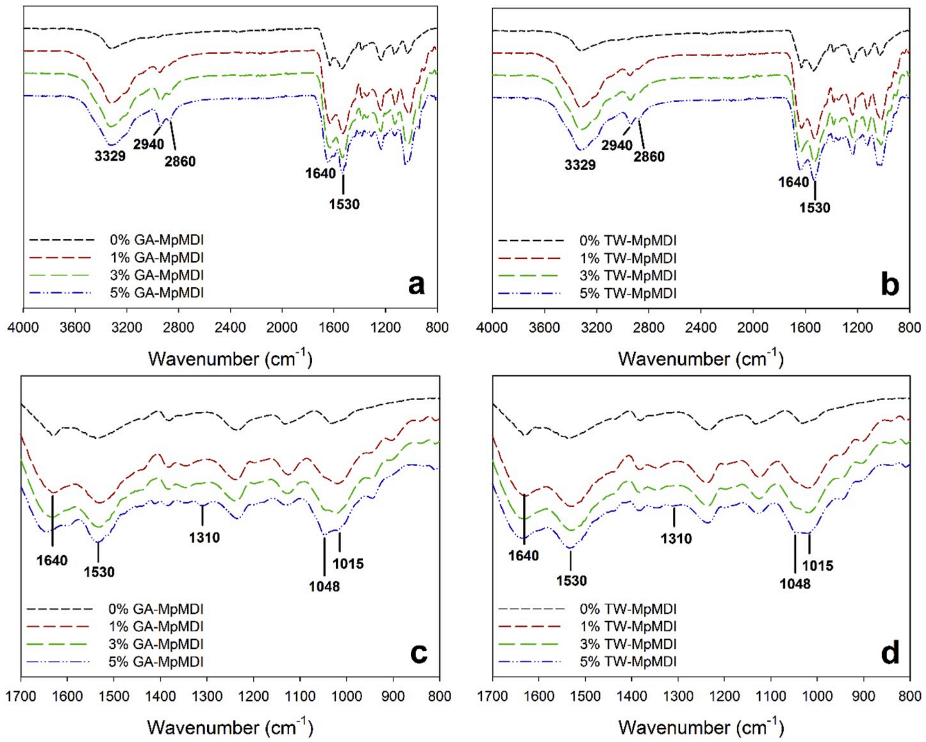

Fig. 6. Typical ATR-FTIR spectra of (a) cured UF/GA-MpMDI, and (b) cured UF/TW-MpMDI at different MpMDI contents; enlarged ATR-FTIR spectra of (c) cured UF/GA-MpMDI, and (d) cured UF/TW-MpMDI at different MpMDI contents.

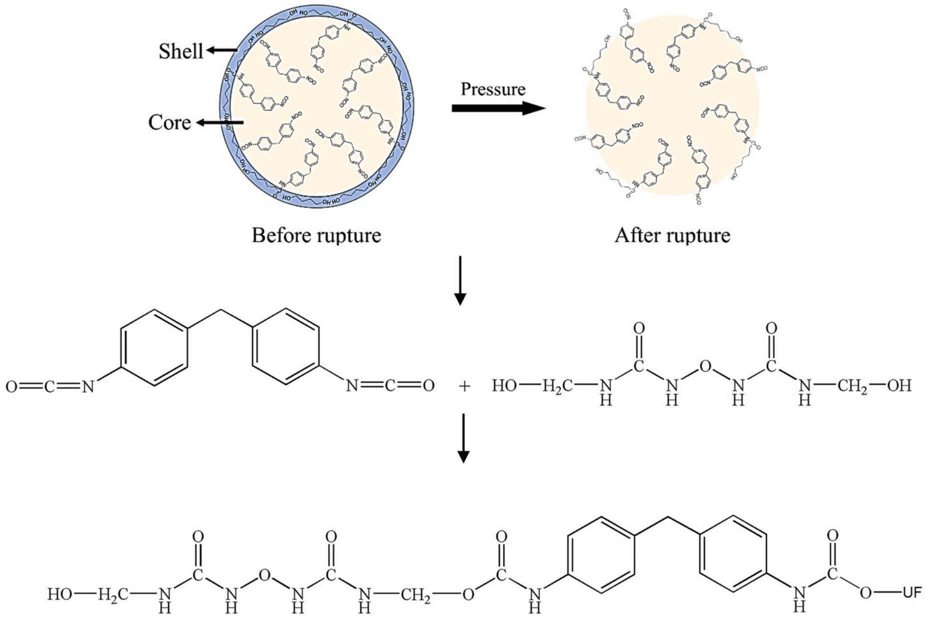

Fig. 7. Possible reaction scheme between MpMDI and UF resins.

respectively. In the fingerprint region, the addition of MpMDI had altered some functional groups of UF resins (Fig. 6c and d). Incorporating 5% of GA- and TW-MpMDI into UF resins shifted the peak of C═O from 1640 cm^{-1} to 1648 cm^{-1}, indicating the formation of urethane bonds from the reaction between –NCO groups and hydroxymethyl groups ($–CH_2–OH$) in the UF resins adhesives [9]. This was confirmed by a decrease in the normalized intensity of C–O of hydroxymethyl end groups of UF resins at 1015 cm^{-1} due to the formation of urethane bonds (Fig. 6c and d), and the normalized intensity of C–N of methylene bridges at 1048 cm^{-1} increased afterward [30]. In addition, C–N of aromatic amine at 1310 cm^{-1} from MpMDI was detected at 5% level of MpMDI. However, in case of 1% and 3% addition of MpMDI, the chemical groups of UF resins did not much change. It was possibly due to the reaction between 1% or 3% of MpMDI and UF resins yielding in less amount of urethane bonds. Therefore the peak was possibly overlapping with the C═O of UF resins at 1640 cm^{-1}.

Fig. 7 shows the possible reaction of between MpMDI and UF resins. Before the shell rupturing, the –NCO groups in the core were not detected because it was covered with the shell. However, after the shell rupturing, the –NCO groups were released for the reaction with UF

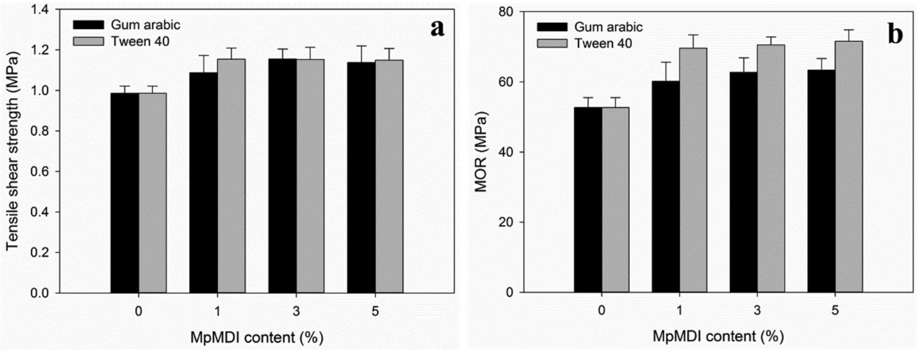

Fig. 8. Properties of plywood bonded with UF/MpMDI adhesives at different MpMDI contents and two different surfactants. (a) TSS and (b) MOR.

Table 2
Duncan multiple range test on properties of plywood bonded with UF/MpMDI adhesives at different MpMDI contents and surfactant types.

Properties	GA-MpMDI content (%)				TW-MpMDI content (%)			
	0	1	3	5	0	1	3	5
Tensile shear strength (MPa)	0.99[a] (B)	1.08 (A)	1.15 (A)	1.14 (A)	0.99 (B)	1.15 (A)	1.15 (A)	1.15 (A)
Modulus of rupture (MPa)	52.69 (B)	60.16 (B)	62.72 (A)	63.31 (A)	52.69 (B)	69.59 (A)	70.53 (A)	71.55 (A)
Formaldehyde emission (mg/L)	1.97 (D)	1.51 (C)	1.22 (B)	0.79 (A)	1.97 (D)	1.23 (C)	1.04 (B)	0.93 (A)

[a] The mean values with the same letter are not significantly different each other at the p value = 0.05.

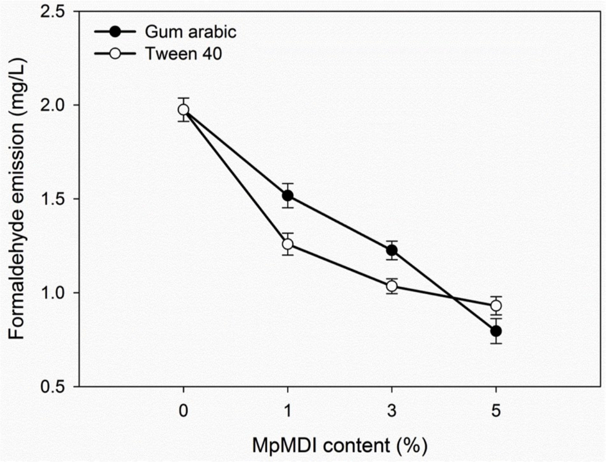

Fig. 9. The FE values of plywood bonded with UF/MpMDI adhesives with different contents of MpMDI and surfactant types.

resins and forming urethane bonds. The formation of urethane bonds was confirmed by ATR-FTIR analysis of the cured UF/MpMDIs (Fig. 6).

3.4. *Properties of plywood*

The adhesion performance of UF/MpMDI adhesives at different MpMDI contents and surfactant types were evaluated in plywood. TSS and MOR values of plywood bonded with UF/MpMDI adhesives are displayed in Fig. 8. In general, plywood bonded with UF/MpMDI adhesives had greater TSS and MOR values than that of the plywood bonded with neat UF resins. Both TSS and MOR of plywood increased the values as a function of MpMDI content. Moreover, plywood bonded with UF/TW-MpMDI adhesives had higher TSS and MOR values than that of UF/GA-MpMDI adhesives. This result shows that the addition of MpMDI into UF resins improves the adhesion performance of UF resins in plywood. These results indicates that the MpMDI probably has been ruptured during hot-pressing of plywood, leading to the formation of urethane bonds by the reaction between the hydroxymethyl groups of UF resins or wood polymers and –NCO groups from MpMDI [31,32]. As shown in Figs. 4, 6 and 7, the –NCO groups appears after rupturing the MpMDI shell, showing the –NCO groups are ready for the reaction with the hydroxymethyl groups of UF resins or wood to form the urethane bonds. Regardless of the type of surfactant, both TSS and MOR values of plywood were improved up to 15 and 30%, respectively, by adding 5% of MpMDI into UF resins.

The improvement on adhesion of UF/TW-MpMDI adhesives could be related to their properties. As presented in Table 1, UF/TW-MpMDI adhesives had higher solids content and viscosity than those of UF/GA-MpMDI adhesives, indicating that the UF/TW-MpMDI adhesives had greater reactivity than those of UF/GA-MpMDI adhesives. DSC analysis confirmed that the T_p values of UF/TW-MpMDI were slightly lower than those of the UF/GA-MpMDI (Fig. 5). However, statistical analysis showed no significant differences between properties of UF/GA-MpMDI and UF/TW-MpMDI adhesives at different contents of MpMDI (Table 2). As displayed in Fig. 6, the chemical groups of UF/MpMDI adhesives does not much changed except an increase in the normalized intensity of C–H stretch at 2940 cm^{-1} and 2860 cm^{-1}, which are assigned to the C–H of 1,4 butanediol and pMDI.

In addition to the adhesion performance, FE is another important parameter for UF resins-bonded panels. Fig. 9 shows the FE values of plywood bonded with UF/MpMDI adhesives as a function of the MpMDI content and surfactant type. Plywood bonded with UF/MpMDI adhesives had lower FE values than the plywood bonded with neat UF resins. The FE values decreased gradually as the MpMDI content increased. Regardless of the surfactant type, the FE values decreased significantly by 54% with the addition of 5% MpMDI into UF resins. Statistical analysis also revealed that 5% addition of MpMDI into UF resins was significantly different from other levels (Table 2). This could be explained by the result of adhesion performance of plywood bonded with UF/MpMDI adhesives, which it increased as the content of MpMDI increased (Fig. 8). In this case, the MpMDI could have ruptured during hot-pressing of plywood, and led to the formation of urethane bonds via the reaction of hydroxymethyl groups of UF resins and –NCO groups of MpMDI, or between hydroxyl groups of wood polymers and –NCO groups. As reported, the hydroxymethyl groups were one of the main sources for formaldehyde emission from UF resins [21]. Therefore, the former was probably responsible for decreasing of the FE values from plywood bonded with UF/MpMDI adhesives.

4. Conclusions

Liquid pMDI was successfully microencapsulated through interfacial polymerization using two types of the surfactant, which was confirmed by LM and FE-SEM. ATR-FTIR spectroscopy detected the urethane bonds in the MpMDI shell. The microscopic observations revealed that TW-MpMDI was spherical and smooth while GA-MpMDI was irregular and rough. The diameter of TW-MpMDI was smaller than those of GA-MpMDI as the agitation rate increased. Regardless of the surfactant types, the agitation rate had greater impact to the diameter of MpMDI than the reaction temperature did. The incorporation of MpMDI into UF resins slightly increased the non-volatile solids content, pH, gelation time, viscosity, and peak temperature of UF/MpMDI adhesives. The chemical groups of UF/MpMDI adhesives slightly changed after the incorporation of MpMDIs prepared by two types of the surfactant. Urethane bonds were detected in UF/MpMDI adhesives from the reaction between the hydroxymethyl groups of UF resins or wood polymers and –NCO groups from MpMDI. As the results, the adhesion performance of plywood bonded with UF/MpMDI adhesives was improved and FE from the panel was reduced as the MpMDI content increased. Statistical analysis suggests that 5% MpMDI addition into UF resins produce better adhesion strength and lower FE from plywood. There is no significant difference in properties between TW-MpMDI and GA-MpMDI in the UF resins. However, it is suggested to use smaller diameter of microcapsules prepared by TW-MpMDI for modification of UF resins to obtain better performance, indicating that 1% TW-MpMDI addition into UF resins was a proper balance between good adhesion and low formaldehyde emission for plywood.

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