Synthesis of polymeric isocyanate microcapsules via interfacial polymerization and their characterisation using spectroscopy and microscopy techniques

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Abstract. Wood adhesives are holding a key in improving the efficiency of using raw materials in the wood-based industry and in durability of the panels during their life in service. Massive progress has been made on research and development of wood adhesives over the past century, but many important challenges are still remaining. In this study, an alternative crosslinker for wood adhesives named microcapsules polymeric 4,4 methane diphenyl isocyanate (M-pMDI) were synthesized at different conditions via interfacial polymerization, and were characterized using spectroscopy and microscopy techniques. Three factors were taken into account to examine the characteristics of M-pMDI, namely isocyanate content, microencapsulation temperature, and microencapsulation agitation rate. Attenuated total reflectance Fourier transform infrared spectroscopy revealed that the isocyanate (−N=C=O) groups of pMDI at 2,250 cm⁻¹ disappeared after microencapsulation due to the reaction of pMDI and ethylene glycol to form urethane (−R−NH−C=O−) linkages at 1,650 cm⁻¹ as microcapsules shell. Digital microscopy and micro confocal raman imaging hyperspectral spectroscopy confirmed the formation of microcapsules and urethane shell. The results showed that concentration of isocyanate remarkably affected the yield of M-pMDI, while microencapsulation temperature and agitation speed influence the formation of microcapsules itself. Preliminary investigation using ATR-FTIR spectroscopy confirmed that free −NCO groups could be released by applying pressure. This study suggested that a combination of 5 mL of pMDI, 60°C of microencapsulation temperature, and 600 rpm of microencapsulation agitation speed could produce M-pMDI with high yield as an alternative cross-linker for wood adhesives in the future.

1. Introduction
Isocyanates are one of the major chemicals in the world since found in 1848 due to their versatility [1,2]. As a wood adhesive, isocyanates are commonly used in two ways. The first one is used as a polyurethane pre-polymer that being used in the wood laminating industry, and last is directly used as the isocyanate in the particleboard industry [3]. Toluene diisocyanate (TDI), Isophorone diisocyanate (IPDI), Hexamethylene diisocyanate (HDI), and Methylene diphenyl isocyanate (MDI) are the mostly used isocyanates. The isocyanates are known very sensitive to moisture, which limits their use and lower storage life [4]. To overcome this, a method called blocking has been developed. 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 [5,6]. However, the use of blocked isocyanates is limited due to their high de-
blocking temperature to release the –NCO groups [7]. Another way is to protect the –NCO groups through microencapsulation.

Microencapsulation is a technique of enclosing specific substances with shell materials via chemical and physical processes [8]. Microcapsules are a type of micro containers with an active chemical that prepared through chemical and physical microencapsulation [9]. The first preparation of microcapsules was recorded at around 1950s, when a group of researcher fabricated dyes microcapsules for copying paper [10]. The isocyanate microcapsules are usually prepared by means of interfacial polymerization which produces uniform size of microcapsules [11]. When the microcapsules rupture, it releases the active –NCO groups and reacts with the main polymer. Hence, the isocyanate microcapsules are good options of using as wood adhesive or a cross-linker. This is due to the similarity of protecting and releasing the –NCO groups as blocked isocyanates.

Recent study shows that isocyanate microcapsules derived from polymeric 4,4-methylene diphenyl isocyanate (pMDI) has been prepared via interfacial polymerization using 1,4-butanediol as shell materials and tween 40 as surfactant [12]. The obtained microcapsules show the free –NCO groups after rupture confirmed by attenuated total reflectance Fourier transform infrared (ATR-FTIR). It was observed that microcapsule size as low as 10 microns could be obtained. Another study produced microcapsules with HDI as a core in a polyurethane shell synthesized via interfacial polymerization of pMDI prepolymer and 1,4-butanediol with size as low as 1.7 microns [13]. The resulting isocyanate microcapsules are widely used as self-healing materials and cross-linker in polymer composites [14]. The common polyols used in the preparation of isocyanate microcapsules are 1,4-butanediol, 1,6-hexanediol, and glycerol [8].

Previous studies report the preparation of isocyanate microcapsules for self-healing materials that involved two separate steps [11,15]: (1) interfacial reaction between isocyanates and polyols to build the urethane shell wall, (2) rinsing and filtration of prepared isocyanate microcapsules. Many factors affecting characteristics of isocyanate microcapsules. The isocyanate content, microencapsulation temperature, microencapsulation agitation rate, type of polyol, and type of surfactant are known to be the main parameter on controlling the characteristics of isocyanate microcapsules. It has been reported that the isocyanate droplets are probably cracked by greater shear forces and interfacial tension that has been created from higher agitation rate. Moreover, higher temperature may swell the microcapsules [12,14]. Further research is needed to develop isocyanate microcapsules that can be used as adhesive, additive, and cross-linker.

This present study aimed to synthesis polymeric isocyanates microcapsules derived from polymeric 4,4-methylene diphenyl isocyanate (pMDI) via interfacial polymerization with ethylene glycol that has a potential to be used as cross-linker for wood adhesives. The microcapsules pMDI (M-pMDI) were produce at different isocyanate contents, different microencapsulation temperatures, and different microencapsulation agitation rates. The M-pMDI characteristics were investigated using spectroscopy and microscopy techniques, including attenuated total reflectance Fourier transform infrared, digital microscope, and micro confocal raman hyperspectral imaging spectroscopy.

2. Materials and Methods

2.1. Materials
Polymeric 4,4-methylene diphenyl isocyanate (pMDI, Koyobond, Indonesia), acetone, and ethylene glycol were used to prepare microcapsules pMDI (M-pMDI). Tween 80 was used as a surfactant to reduce the surface tension during interfacial polymerization.

2.2. Methods

2.2.1. Preparation of microcapsules pMDI (M-pMDI)
Three parameters were taken into account in the preparation of M-pMDI, namely amount of isocyanate, microencapsulation temperature, and microencapsulation agitation speed. Schematic diagram of microencapsulation of pMDI is presented in Figure 1.
First, a set of different isocyanate contents such as 3, 5, 7, and 9 mL was used to prepare M-pMDI. The isocyanate was diluted in acetone to make an 80% of concentration prior to microencapsulation. Around 50 g of ethylene glycol was poured into a beaker glass and 0.05 g of tween 80 was added subsequently. Furthermore, the diluted pMDI was dropped into the mixture at a dropping rate of 5.0 mL/min. The microencapsulation was completed after stirring at 600 rpm for 30 min at temperature of 60°C. The mixture was subsequently filtered and then oven dried for 24-h at 60°C to obtain the M-pMDI.

Second, different microencapsulation temperatures such as 25, 40, 60, and 80°C were used to prepare M-pMDI. Around 5 mL of pMDI was diluted in acetone to make an 80% of concentration prior to microencapsulation. Approximately 50 g of ethylene glycol was poured into a beaker glass and 0.05 g of tween 80 was added subsequently. Furthermore, the diluted pMDI was dropped into the mixture at a dropping rate of 5.0 mL/min. The microencapsulation was completed after stirring at 600 rpm for 30 min, and at different temperatures of 25, 40, 60, and 80°C. The mixture was subsequently filtered and then oven dried for 24 hours at 60°C to obtain the M-pMDI.

Third, different microencapsulation agitation rates such as 300, 400, 500, and 600 rpm were also used to prepare M-pMDI. Same as previous, 5 mL of pMDI was diluted in acetone to make an 80% of concentration prior to microencapsulation. Then, 50 g of ethylene glycol was poured into a beaker glass and 0.05 g of tween 80 was added subsequently. The diluted pMDI was then dropped into the mixture at a dropping rate of 5.0 mL/min. The microencapsulation was completed after stirring at different agitation speed of 300, 400, 500, and 600 rpm for 30 min, and at temperatures of 60°C. The mixture was subsequently filtered and then oven dried for 24 hours at 60°C to obtain the M-pMDI.

2.2.2. M-pMDI characterization
The yield of M-pMDI was calculated after oven dried by dividing the dried mass of M-pMDI with the mass of pMDI. Functional groups of each M-pMDI were recorded using ATR-FTIR spectroscopy (Spectrum Two, Perkin Elmer, United States). A small amount of sample was placed in ATR-FTIR, and was scanned in the range of 400-4000 cm⁻¹ and at room temperature. In addition, pure pMDI was also used as the control. Images of M-pMDI were recorded by putting M-pMDI sample on to a slide glass and covered with a cover glass with a help of digital microscope (VHX 6000, Keyence, Japan) at 500 times of magnification with Dual-Light High-Magnification Zoom Lens VH-Z250T. Micro confocal raman hyperspectral imaging spectrometer (LabRAM HR Evolution, Horiba, Japan) was used to confirm the formation of M-pMDI. M-pMDI sample was put on the slide glass, and the image was capture using an objective lens at 100 times of magnification. The sample image then was bombarded with a laser at a wavelength of 785 nm. The measurement was performed at raman shift of 200-4000 cm⁻¹ and at room temperature.
3. Results and Discussion

3.1. Effect of isocyanate content on characteristics of M-pMDI

The yield of M-pMDI increased as the amount of isocyanate raised from 3 mL to 5 mL (Table 1). But, as the amount of isocyanate was greater than 5 mL, the yield of M-pMDI decreased remarkably. This is probably due to coagulation of pMDI at 7 and 9 mL of isocyanate. Different phases between oily pMDI and aqueous ethylene glycol are the main reason for the coagulation [16]. Insufficient amount of tween 80 surfactant to reduce the surface tension probably also played some part on coagulation of pMDI that eventually decreased the yield of M-pMDI.

Table 1. Yield of M-pMDI at different isocyanate contents prepared at 60°C and 600 rpm

| Isocyanate content (mL) | Mass of pMDI (g) | Mass of M-pMDI | Yield (%) |
|------------------------|------------------|----------------|----------|
| 3                      | 2.40             | 0.16           | 6.87     |
| 5                      | 4.09             | 0.83           | 20.22    |
| 7                      | 5.91             | 0.95           | 16.13    |
| 9                      | 7.88             | 1.09           | 13.85    |

The pure pMDI was dark brown and liquid. The microencapsulation of pMDI resulted M-pMDI with a yellow color (Figure 2a). The morphology of M-pMDI was analyzed using microscopy technique. Digital microscope displays example of M-pMDI produced with 5 mL of isocyanate at 60°C of microencapsulation temperature and 600 rpm of agitation speed (Figure 2b). The spherical isocyanate microcapsules have been formed via interfacial polymerization with observable aggregation. This observation was in agreement with the published works [11,12].

The functional groups of pMDI and M-pMDI were investigated using spectroscopy technique. ATR-FTIR spectroscopy detected the change in functional groups of pMDI after microencapsulation into M-pMDI (Figure 3a). Typical strong peaks at 2250, 1770, and 1525 cm⁻¹ were observed only in pure pMDI which is assigned to vibration of –N=C=O groups [9]. Those peaks disappeared after microencapsulation due to the reaction between –NCO groups of pMDI and –OH groups of ethylene glycol to form urethane (–R–NH–C=O–) linkages at 1,650 cm⁻¹, which was detected in all M-pMDI. In addition, the vibration of–CH at 2948 and 2880 cm⁻¹ were observed in M-pMDI which was attributed...
to the C–H of urethane linkages. Broad peak at 3300 cm\(^{-1}\) was the –OH groups which originated from incorporation ethylene glycol. Micro confocal raman hyperspectral imaging spectroscopy revealed the formation of urethane (–R–NH–C=O–) linkages at 1625 cm\(^{-1}\) and the C–H of urethane at 2920 cm\(^{-1}\) (figure 3b). The raman spectra was obtained by bombarded a laser with 785 nm of wavelength onto the shell of M-pMDI. This confirmed that the shell of microcapsules was built by urethane linkages from the reaction of –NCO groups of pMDI and –OH groups of ethylene glycol.

![Figure 3](image-url)

**Figure 3.** (a) Typical ATR-FTIR spectra of pMDI and M-pMDI at different isocyanate contents, (b) formation of microcapsules and raman spectra of M-pMDI 5 mL detected by micro confocal raman hyperspectral imaging spectroscopy at 100 times magnification

3.2. **Effect of microencapsulation temperature on M-pMDI properties**

Influence of microencapsulation temperature on M-pMDI characteristics was also examined. Table 2 presents the yield of M-pMDI prepared with 5 mL under 600 rpm of agitation speed and at different microencapsulation temperature. The yield of M-pMDI slightly increased by 19.5% as the microencapsulation temperature increased from 25°C to 60°C. This shows that temperature plays a quite significant role on microencapsulation of pMDI.

| Microencapsulation temperature (°C) | Mass of pMDI (g) | Mass of M-pMDI (g) | Yield (%) |
|-----------------------------------|------------------|--------------------|-----------|
| 25                                | 4.31             | 0.14               | 3.19      |
| 40                                | 4.34             | 0.15               | 3.48      |
| 60                                | 4.30             | 0.16               | 3.81      |
| 80                                | 4.28             | 0.15               | 3.59      |

The M-pMDI morphology was a quite similar to the previous section. Figure 4a displays an example of M-pMDI prepared with 5 mL of pMDI at 40°C and 600 rpm. A yellow color of microcapsules was observed similar to M-pMDI prepared at different isocyanate contents. Figure 4b shows image of M-pMDI produced with 5 mL of isocyanate at 40°C of microencapsulation temperature and 600 rpm of agitation speed provided by digital microscope. Spherical M-pMDI have been formed via interfacial polymerization with observable aggregation similar to M-pMDI prepared at different isocyanate contents. This observation was in agreement with the published works [11,12].
Figure 4. (a) Example of M-pMDI prepared with 5 mL of pMDI at 40°C and 600 rpm. (a) Image of the same M-pMDI sample captured by digital microscope at 500 times magnification

The chemical structures of pMDI and M-pMDI were also investigated using spectroscopy technique. ATR-FTIR spectroscopy detected the change in functional groups of pMDI after microencapsulation into M-pMDI (Figure 5a). Similar to M-pMDI prepared at different isocyanate content, three strong peaks at 2250, 1770, and 1525 cm\(^{-1}\) were observed only in pure pMDI, which is assigned to vibration of –N=C=O groups [9]. That peaks disappeared after microencapsulation due to the reaction between –NCO groups of pMDI and –OH groups of ethylene glycol to form urethane (–R−NH−C=O−) linkages at 1650 cm\(^{-1}\), which was detected in all M-pMDI. In addition, the vibration of –CH at 2948 and 2880 cm\(^{-1}\) were observed in M-pMDI which was attributed to the C–H of urethane linkages. Broad peak at 3300 cm\(^{-1}\) was assigned to –OH groups which originated from ethylene glycol. Micro confocal raman hyperspectral imaging spectroscopy revealed the formation of urethane (–R−NH−C=O−) linkages at 1625 cm\(^{-1}\) and the C–H of urethane at 2920 cm\(^{-1}\) as microcapsules shell (figure 5b). This confirmed that the shell of microcapsules was built by urethane linkages from the reaction of –NCO groups of pMDI and –OH groups of ethylene glycol.

Figure 5. (a) Typical ATR-FTIR spectra of pMDI and M-pMDI at different microencapsulation temperatures, (b) formation of microcapsules and raman spectra of M-pMDI 60°C detected by micro confocal raman hyperspectral imaging spectroscopy at 100 times magnification
3.3. Effect of microencapsulation agitation rate on M-pMDI characteristics

Effect of microencapsulation agitation rate on M-pMDI characteristics was also investigated. The yield of M-pMDI prepared with 5 mL at 60 °C and at different microencapsulation agitation speed is presented in Table 3. The yield of M-pMDI remarkably increased by 60.9% as the agitation speed rose from 300 to 600 rpm. By contrast to microencapsulation temperature, agitation speed plays significant role on microencapsulation of pMDI. The isocyanate droplets are possibly broken by greater shear forces and interfacial tension that has been created from higher agitation rate while higher temperature may swell the microcapsules [12,14].

| Microencapsulation agitation rate (rpm) | Mass of pMDI (g) | Mass of M-pMDI (g) | Yield (%) |
|----------------------------------------|------------------|--------------------|-----------|
| 300                                    | 4.30             | 0.40               | 9.47      |
| 400                                    | 4.31             | 0.41               | 9.56      |
| 500                                    | 4.30             | 0.51               | 11.93     |
| 600                                    | 4.30             | 0.65               | 15.23     |

Morphology of M-pMDI prepared at different agitation rates was a quite similar to the M-pMDI produced with different isocyanate contents and at different temperatures. Figure 6a displays an example of M-pMDI prepared with 5 mL of pMDI at 60°C and 300 rpm. A yellow color of microcapsules was observed similar to M-pMDI prepared at different isocyanate contents and at different temperatures. Figure 6b shows image of M-pMDI produced with 5 mL of isocyanate at 60°C of microencapsulation temperature and 300 rpm of agitation speed provided by digital microscope. Spherical M-pMDI have been formed via interfacial polymerization with observable aggregation similar to M-pMDI prepared at different isocyanate contents. This observation was in agreement with the published works [11,12].

**Figure 6.** (a) Example of M-pMDI prepared with 5 mL of pMDI at 60°C and 300 rpm. (a) Image of the same M-pMDI sample captured by digital microscope at 500 times magnification

ATR-FTIR spectroscopy detected the change in functional groups of pMDI after microencapsulation into M-pMDI (Figure 7a). Similar to M-pMDI prepared at different isocyanate content and different temperatures, three strong peaks at 2250, 1770, and 1525 cm\(^{-1}\) were observed only in pure pMDI, which is assigned to vibration of \(-\text{N}=\text{C}=\text{O}\) groups [9]. The peaks disappeared after microencapsulation due to the reaction between \(-\text{NCO}\) groups of pMDI and \(-\text{OH}\) groups of ethylene glycol to form urethane \((-\text{R}−\text{NH}−\text{C}=\text{O}−)\) linkages at 1650 cm\(^{-1}\), which was detected in all M-pMDI. In addition, the vibration of \(-\text{CH}\) at 2948 and 2880 cm\(^{-1}\) were observed in M-pMDI which was attributed to the C−H of urethane...
linkages. Broad peak at 3300 cm\(^{-1}\) was assigned to \(--\text{OH}\) groups which originated from ethylene glycol. The formation of urethane (\(--\text{R}\--\text{NH}\--\text{C}==\text{O}\)--) linkages at 1625 cm\(^{-1}\) and the C–H of urethane at 2920 cm\(^{-1}\) as microcapsules shell was detected by micro confocal raman hyperspectral imaging spectroscopy (figure 7b). This confirmed that the shell of microcapsules was built by urethane linkages from the reaction of \(--\text{NCO}\) groups of pMDI and \(--\text{OH}\) groups of ethylene glycol.

![Figure 7](image)

**Figure 7.** (a) Typical ATR-FTIR spectra of pMDI and M-pMDI at different microencapsulation temperatures, (b) formation of microcapsules and raman spectra of M-pMDI 600 rpm detected by micro confocal raman hyperspectral imaging spectroscopy at 100 times magnification

![Figure 8](image)

**Figure 8.** Pre-liminary investigation of M-pMDI as cross-linker for wood adhesives using ATR-FTIR

3.4. Potential application of M-pMDI
The M-pMDI were successfully produced via interfacial polymerization between pMDI and ethylene glycol with the help of Tween 80 as surfactant. Figure 8 displays the ATR-FTIR spectra of M-pMDI prepared with 5 mL of isocyanate, at 60\(^\circ\)C, and under 600 rpm of agitation rate. The spectra show an interesting result revealing that the core of M-pMDI contained active \(--\text{NCO}\) groups. This free \(--\text{NCO}\) groups was detected at 2250 cm\(^{-1}\) after cracking the shell of M-pMDI using pressure of ATR-FTIR.
instrument. The releasing of free –NCO groups was followed by disruption of M-pMDI urethane shell. The ATR-FTIR spectra showed that peak of urethane (−R−NH−C=O−) linkages at 1650 cm\(^{-1}\) disappeared after cracking of M-pMDI shell. In addition, the releasing of free –NCO groups also supported by a new peak of C=O at 1770 cm\(^{-1}\) which was previously only detected in pure pMDI. Based on this pre-liminary investigation, M-pMDI have a potential to be used as cross-linker for wood adhesives, such as formaldehyde-based adhesives and bio-based adhesives. Figure 9 depicts the illustration on how M-pMDI can be used as cross-linker for wood adhesives.

![Illustration of potential application of M-pMDI as cross-linker for wood adhesives](image)

**Figure 9.** Illustration of potential application of M-pMDI as cross-linker for wood adhesives

4. Conclusion
Polymeric isocyanate microcapsules derived from Polymeric 4,4-methylene diphenyl isocyanate were prepared via interfacial polymerization with ethylene glycol. The resulting M-pMDI has a yellow color and spherical form with observable aggregation. The yield of M-pMDI remarkably increased as the isocyanate content, microencapsulation temperature, and microencapsulation agitation rate increased to some degrees. ATR-FTIR and micro confocal raman hyperspectral imaging spectroscopy enabled to detect the change of chemical structure of M-pMDI by assessing their functional groups. The –NCO groups of pure pMDI was not detected after microencapsulation due to the covering effect of urethane shell formed from the reaction of –NCO groups of pMDI and –OH groups of ethylene glycol. Images from digital microscope and micro confocal raman hyperspectral imaging spectroscopy revealed the formation of the urethane shell of M-pMDI. The pre-liminary investigation of M-pMDI using ATR-FTIR spectroscopy suggested that M-pMDI prepared with 5 mL isocyanate, at 60°C of microencapsulation temperature, and 600 rpm of microencapsulation agitation rate could be used as cross-linker for wood adhesives.

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