

Evaluation of Bio/pMDI Wood Adhesives

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

I would like to state I am the sole author of the Chapter 1, 2 and 4.

Chapter 3 is an unpublished manuscript *Behavior of water/pMDI Emulsion Adhesive on Bonding Wood Substrate with Varied Surface Properties*, which is co-authored with Dr. Li Yu in result and discussion and reviewed by my supervisor Professor Boxin Zhao and Julien Mesnager et al. from Ecosynthetix.

Abstract

With the increasing concerns about formaldehyde emissions from wood-based panels and the demands of the sustainable products, the potential of synthetic wood resins derived from biomass resources has sparked enormous interest. To date, extensive efforts have been devoted to investigating the mechanism, the properties, and the modification approach of the bio-adhesives. To overcome the limitations of pure bio-adhesives (low reactivity, low moisture resistance, and biodegradation), many approaches have been developed to partially replace the bio-polymer with synthetic thermosetting adhesives. In this project, a functional experimental grade binder, made from the reactive extrusion modification process of biopolymers with other reagents, is used as a co-binder in combination with polymeric methylene diphenyl diisocyanate (pMDI) resin, to study the resulting performance of the system for wood adhesive applications.

To evaluate the influence of the experimental grade biopolymer binder on the performance of the pMDI adhesive, a pMDI adhesive blended with water was first investigated. The effect of water content on emulsion morphology and viscosity was characterized. For bonded samples, formulations obtaining the highest bonding strength of the water/pMDI adhesives was determined by comparing the pull-off stress and the lap-shear stress. To further improve the bonding performance, the wood substrate was modified by the silane coupling agent, (3-aminopropyl) triethoxysilane (APTES). The penetration

depth of pMDI in the different wood substrates (neat wood, 1wt% APTES-treated wood, 3wt% APTES-treated wood) was accurately determined. These studies indicate that both strong interactions between the adhesives and wood substrate, and a certain level of penetration of the adhesives, are required for the good bonding performance of the water/pMDI adhesives.

The biopolymer/pMDI adhesives were prepared and investigated based on the protocols from the industry partner Ecosynthetix. By comparing the biopolymer/pMDI adhesives with the water/pMDI adhesives, the effect of the biopolymer to the pMDI was determined. The biopolymer can work as a thickener, emulsifier of the system to reduce the dosage of pMDI. In terms of bonding performance, the bonding strength of the biopolymer/pMDI adhesive is comparable with the highest stress achieved by water/pMDI resin, indicating the experimental grade biopolymer can be applied as an effective wood adhesive binder to partially replace pMDI without reducing the overall bonding performance.

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List of Abbreviations

APTES	(3-aminopropyl) triethoxysilane
BA	Butyl acrylate
CLSM	Confocal laser scanning microscopy
EPI	Emulsion polymer isocyanate
FM	Fluorescence microscopy
KLPF	Kraft lignin-based phenol-formaldehyde resin
LM	Light microscopy
MA	Maleic anhydride
MDF	Medium density fiberboard
MDI	Methylenediphenyl diisocyanate
MF	Melamine-formaldehyde
MSPI	Maleic anhydride-grafted soy protein isolate
MUF	Melamine-urea-formaldehyde
NaHSO ₃	Sodium bisulfite
OCC	Old corrugated container
OSB	Oriented strand board
PB	Particleboard
PF	Phenol-formaldehyde
pMDI	Polymeric diphenylmethane diisocyanate
PVA	Polyvinyl alcohol
PVAc	Poly vinyl acetate
SEM	Scanning electron microscopy
SPI	Soy protein isolate
SWA	Starch-based wood adhesives

TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TMSP	Trypsin-modified soy proteins
UF	Urea-formaldehyde
VAc	Vinyl acetate
WBPs	Wood-based Panels

Chapter 1. Introduction

Wood-based panels (WBPs) are composite products made by bonding wood materials (chips, fibers, veneer, particles, etc.) with various adhesives [1], [2]. Some types of WBPs like particleboard (PB), oriented strand board (OSB), medium density fiberboard (MDF) are widely used in furniture manufacture and building construction [2]. These interior-grade panels made by formaldehyde-based adhesives (urea-formaldehyde, melamine-urea-formaldehyde and phenol-formaldehyde) often become sources of formaldehyde emissions, as the incompletely curing of the adhesive [1]. Formaldehyde has been classified as a known human carcinogen by the International Agency for Research on Cancer since 2012 [3]. In many countries, standards have been published to limit the formaldehyde emissions from panel products. In the U.S., the formaldehyde emission limitation for particleboard is 0.09 ppm, and for MDF is 0.11 ppm [4]. In Europe, the highest permitted limit for particleboard is 6.5 mg/100 g dry board, for MDF is 7.0 mg/100 g dry board, and for OSB is 8 mg/100 g board (E1 class) [5], [6].

To meet these strict regulations, formaldehyde scavengers (“catchers”) can be applied to decrease the free formaldehyde, but this usually leads to a higher cost [7]. Thus, researchers are seeking to develop formaldehyde-free WBPs based on sustainable and renewable materials such as biopolymers [1], [8]. However, most biopolymers (lignin, starch, protein, etc.) have limitations like low reactivity, low water or moisture resistance,

and pre-modification required [9], and so it is necessary to blend the biopolymer with other crosslinkers or synthetic resins to improve their properties. Among the conventional resins for WBPS, polymeric 4,4-diphenylmethane diisocyanate (pMDI) is a formaldehyde-free adhesive and has great compatibility to biopolymers [1]. Therefore, in this project, a new biopolymer-pMDI blend adhesive which contains an experimental grade biopolymer binder and the pMDI resin was investigated to evaluate the possibility of utilizing the bio-based binder as an efficient wood adhesive co-binder. In Chapter 2, a literature review is presented which briefly reviews the background of the wood adhesive and introduces several types of adhesives.

To achieve the objective, several studies were pursued and presented in this thesis. In Chapter 3, the pMDI adhesive is firstly investigated as a baseline. In this study, an alternative approach to utilizing pMDI resin is explored: preparing the water/pMDI emulsions first, then applying the adhesive emulsion to bond the wood surfaces. The optimum water content of the water/pMDI adhesive is determined based on the emulsion properties and the bonding strength. Then a silane coupling agent APTES is utilized to modify the surface of the wood substrates and further improve the bonding strength. Finally, the adhesive penetration depth is characterized to determine the relationship between adhesive penetration and bonding strength.

In addition, the effect of the experimental grade biopolymer to the pMDI adhesive was studied under the guidance of Ecosynthetix, which is confidential and not included

here. In Chapter 4, concluding remarks are presented to summarize the determinations of this thesis and provide recommendations for future work.

Chapter 2. Literature Review

Wood adhesives are defined as substances which are able to bond wood materials together by surface attachment [10]. Knowledge and use of wood adhesives are not new. For many centuries, natural adhesives such as animal glue and hide glue were widely utilized in furniture construction [11]. However, due to their low resistance to moisture and damp conditions, natural adhesives have been gradually replaced by synthetic wood resins which were first introduced in early 1930's and rapidly developed during World War II [12]. Synthetic wood resins are man-made polymers which have similar physical properties as natural adhesives but can be adjusted to meet some other woodworking requirements such as water-resistance, durability and strength [13].

The synthetic wood resin can be divided into two categories: thermoplastic adhesives and thermosetting adhesives. The thermoplastic adhesives such as polyvinyl acetate emulsions (white glue) and hot melt glues usually solidify through the loss of dispersing solvent and do not undergo chemical reactions, and thus can be readily reversed by heating. Thus, they are most commonly applied in furniture and cabinetry assembly, but not in WBPs manufacture [14]. Thermosetting adhesives, such as formaldehyde-based resins, solidify by undergoing an irreversible polymerization reaction during the curing process. They have better durability, strength performance than thermoplastic adhesives and therefore widely used as adhesives for WBPs [12], [13].

2.1. Conventional Thermosetting Wood Adhesives

The most predominantly used thermosetting adhesives for WBPs are formaldehyde-based adhesives, such as urea-formaldehyde (UF), phenol-formaldehyde (PF), melamine-formaldehyde (MF), and isocyanate-based resins, such as pMDI resin [1], [14]. Based on their different properties, each kind of resin has been applied to fabricate different kinds of WBPs (plywood, PB, OSB, MDF, etc.)

2.1.1. Urea-formaldehyde Resin (UF)

Urea-formaldehyde resins are probably the most widely used thermosetting resin for WBPs, 68% of UF resins produced in the world is consumed to fabricate MDF and particleboard, while 23% is used in interior grade plywood manufacturing [1]. The UF resin is build up by the condensation polymerization of urea and formaldehyde, which occurs in two stages: the alkaline condensation and the acid condensation [6], [15]. In the first alkaline condensation, the urea and formaldehyde react at room temperature to form mono-, di-, and tri-methylolureas (shown in Figure **2.1a**) [6]. In this stage, the products have low molecular weight and are still water soluble. To further increase the molecular weight, the acid condensation stage is necessary. The suggested curing agents in acid condensation include boric acid, phosphoric acid, acid sulfates, hydrochlorides. However, the ammonium chloride and ammonium sulfate are the most widely used curing agents [6], [16], [17]. In acid conditions, the molecules contain methylol end groups could continue

the reaction to build networks and harden the resin (Figure 2.1b) [6].

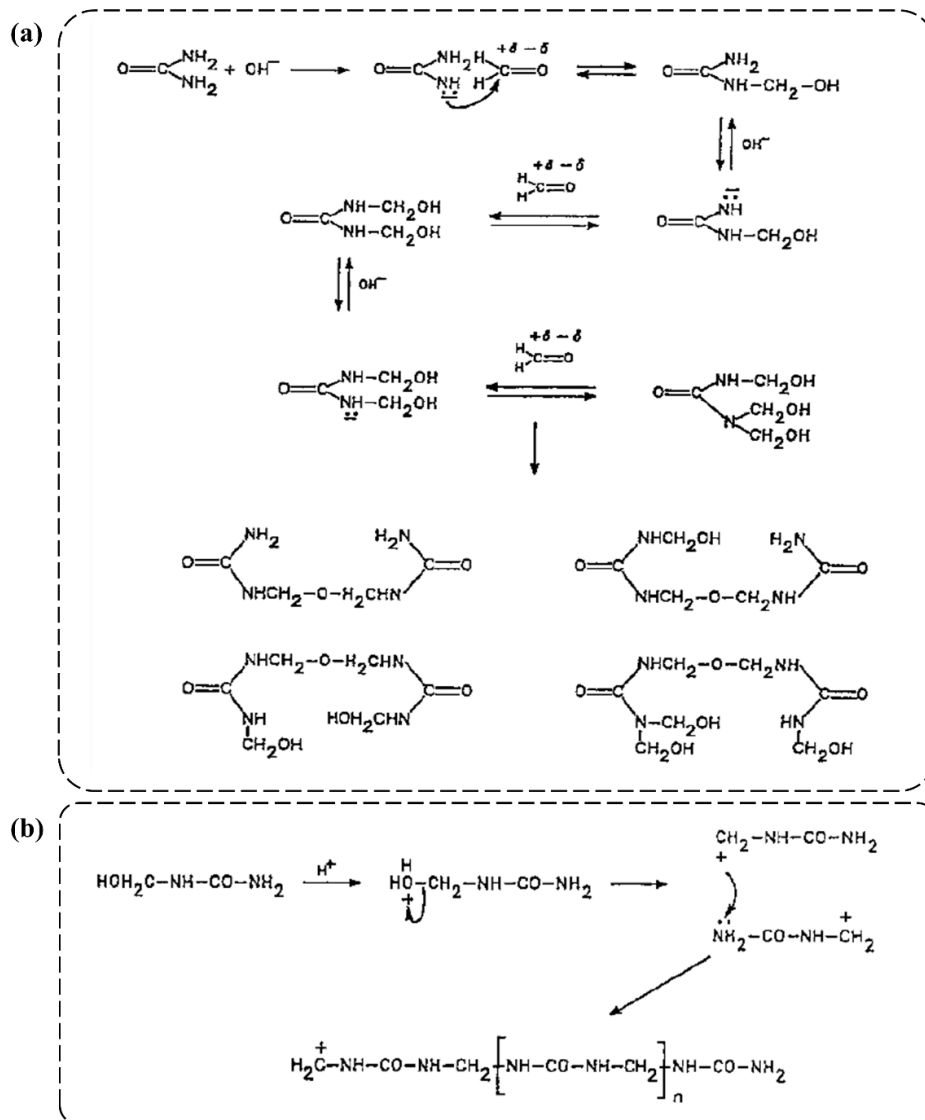


Figure 2.1. The reaction between urea and formaldehyde in (a) alkaline conditions and (b) acid conditions [6]. *Reproduced with permissions from Taylor & Francis Group.*

The properties of the UF strongly depend on the reaction conditions. The average crosslink density of the final resin can be adjusted by the amount of the curing agents. To harden the resin, a large amount of acidic curing agent is added to lower the pH value, increase the cross-linking degree of the resin [15]. The formaldehyde emission from the

UF can be dramatically reduced by decreasing the urea/formaldehyde ratio from 1:1.45 to 1:1.2 or lower (shown as Table 2.1) [6]. This can reduce the unreacted formaldehyde present in the resin but will not have an effect on the formaldehyde formed by hydrolysis of the aminomethylene bond.

Table 2. 1. Comparison of Particleboard Prepared with UF Resins of Various Molar Ratios [6]. *Reproduced with permissions from Taylor & Francis Group.*

Urea/ formaldehyde molar ratio	Approximate density (g/cm ³)	Internal bond (MPa)	Percent water swelling (2 h)	Percent HCHO released, perforator method (mg HCHO/100 g board)
1:1.4-1.5	0.680	0.7-0.8	4	50-70
1:1.3-1.35	0.680	0.6-0.7	4-5	25-30
1:1.1-1.25	0.680	0.45-0.55	5	4-20

The UF adhesives have several advantages which makes them suitable for industrial application, such as initial water solubility, nonflammability, good thermal properties, hardness, light color, and easy adaptability to a variety of curing conditions. However, the greatest disadvantage of the UF resins is that the aminomethylene bond is hydrolysable at high temperature and humidity conditions [15], which will lead to the loss of bonding strength, and long-term formaldehyde emission.

2.1.2. Melamine-formaldehyde Resin (MF)

Melamine-formaldehyde resins are one of the most used adhesives for exterior and semi-exterior wood panels because of their excellent water and weather resistance. The mechanism of the condensation reaction between melamine and formaldehyde has some

similarities to the urea-formaldehyde reaction, with important differences (Figure 2.2) [6]. The amino group of melamine is firstly attacked by formaldehyde to form methylol compounds. Different from the reaction with urea, the formaldehyde can react easily and completely with melamine; each melamine can accept up to two molecules of formaldehyde. The further cross-linking reaction forms methylene and ether bridges, increasing the molecular size of the resin rapidly and producing the desired insoluble and infusible MF resins [6], [18]. Another important difference from UF is that the condensation reaction of MF can occur in acid, neutral or even slightly alkaline conditions [18], which can simplify the curing process and readily adapt to the WBPs applications.

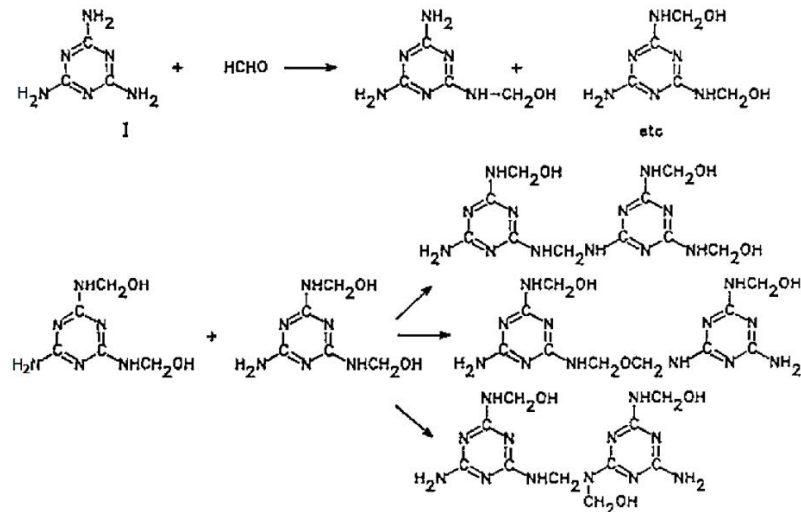


Figure 2.2. Methylation and subsequent condensation reactions of MF [6]. *Reproduced with permissions from Taylor & Francis Group.*

The hydrolysis product of the melamine during the condensation reaction, should be noted. The hydrolysis products of the melamine (ammelina, ammelide, and cyanuric acid) are generated as the amino groups of the melamine are being gradually replaced by

hydroxyl groups. These molecules are very undesirable by-products of the melamine manufacture, and have a catalytic effect on the MF resin, due to their acidic nature [19]. If present in the crude melamine, the hydrolysis products could be removed by alkali wash and/or crystallization of the melamine [6]. The chemical bond between the nitrogen of the melamine is much stronger than those of urea, because of the conjugated double bonds of the quasi-aromatic triazine ring of the melamine: this leads to the characteristic water resistance of the MF [20], [21]. Since melamine and formaldehyde can react completely and form non-hydrolysable bonds in the resin, the MF resin has less formaldehyde emission than UF, and so products composed of MF can usually meet the E1 class of formaldehyde emission regulations in Europe [20].

As the cost of melamine is relative high, copolymers of melamine-urea-formaldehyde (MUF) are generally used to reduce the cost of MF resin [22]. In MUF resin, the relative mass proportions of melamine to urea is generally in the range of 50:50 to 30:70 [6]. By carefully controlling this proportion, reduced costs can be achieved with similar performance to MF.

2.1.3. Phenol-formaldehyde Resin (PF)

Phenol-formaldehyde resins are the oldest kind of synthetic polymers, and widely used in both laminations and composites such as OSB, softwood plywood, exterior grade panels, because of their outstanding durability, good adhesion to wood, high strength, and

excellent thermal stability [8]. Based on their formaldehyde/phenol (F/P) ratio and the polymerization conditions, the pre-polymer can be classified into two types: novolac and resole resins [23]. The novolac resins are made with phenol and formaldehyde by F/P ratio at 0.5 to 0.8 and under acidic condition (pH around 4 to 7). This kind of oligomers is generally not used for wood bonding as they display low water solubility and high acidity [6]. Resole resins are generally made using alkali hydroxides with F/P ratio at 1.0 to 3.0 and pH at 7 to 13, and are utilized for WBPs applications because they provide a soluble adhesive and have good wettability to the wood surface [24].

The mechanism of preparing resole resins is shown in Figure 2.3, wherein a reaction of base-activated phenol with formaldehyde is involved [14]. In phenol structure, the *ortho* and *para* positions are nucleophilic enough to attack the electrophilic formaldehyde. By the addition of formaldehyde, hydroxymethyl molecules are generated, which react with another hydroxymethyl group to form the methylene-bridged dimer [25]. In basic conditions, the addition of formaldehyde to phenol is a rapid step, while the following conversion of the hydroxymethyl derivatives to oligomers is a slow step. These low-molecular-weight oligomers have good water solubility and lead to the good processability of the PF. After being applied to the wood, these oligomers can further cross-link with others, build up polymer backbone and cure to the final adhesive when provided with sufficient heating [14].

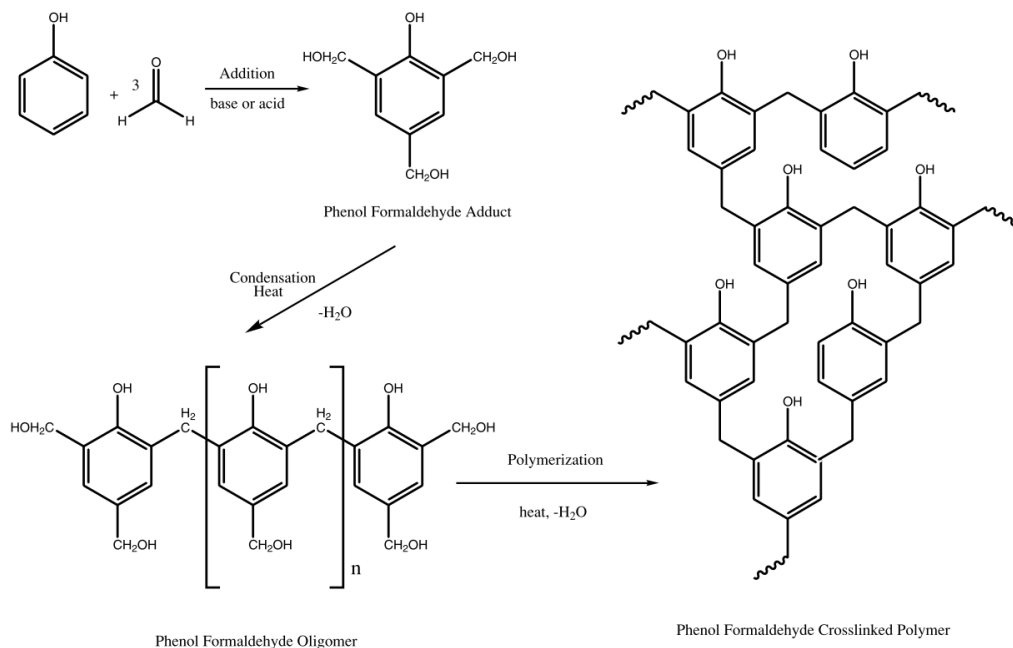


Figure 2.3. Phenol-formaldehyde chemistry under the basic conditions [14]. *Reproduced with permissions from Taylor & Francis Group.*

2.1.4. Polymeric methylene diphenyl diisocyanate Resin (pMDI)

Polymeric methylene diphenyl diisocyanate resins (pMDI) are increasingly used in WBP industry, due to their high reactivity and efficiency. Counterintuitively, pMDI is not the polymeric of methylenediphenyl diisocyanate (MDI): it is produced by the condensation polymerization of formaldehyde and aniline with hydrochloric acid as catalyst, and then undergoes the phosgene reaction to convert the amino groups into isocyanate. After distillation to isolate the 4,4'-MDI, the remaining residue is known as pMDI [26]. Thus, the pMDI is a mixture which often contains diisocyanate monomer, and the complex oligomeric with different polymerization degree (shown in Figure 2.4) [6].

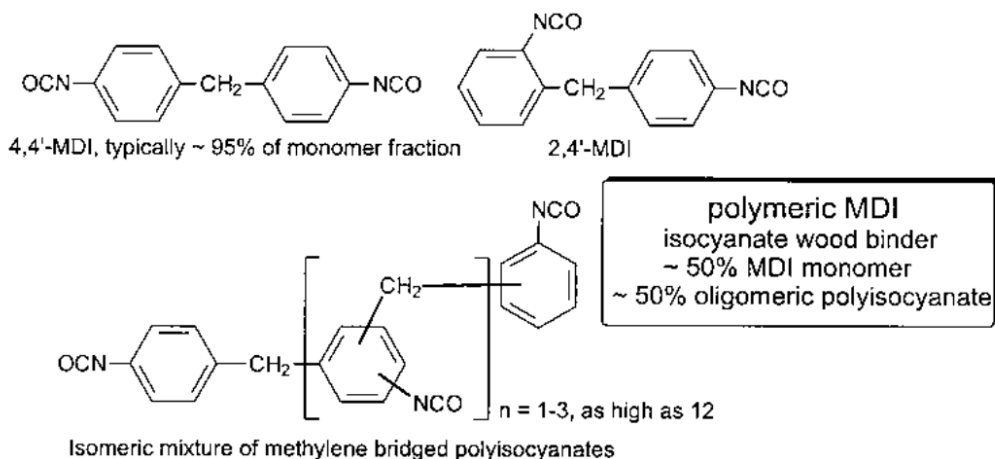


Figure 2.4. The composition of pMDI resin as the wood binder [6]. *Reproduced with permissions from Taylor & Francis Group.*

The isocyanate group in the pMDI has high reactivity to the compounds with "active" hydrogen, such as amines, alcohols, phenols, and water. The general order of relative reactivity is that primary and secondary amines are typically most reactive, followed by primary alcohols, water, secondary alcohols, and phenols [6]. As shown in Figure 2.5, water is necessary for the cross-linking reaction of the pMDI resin. Indeed, the isocyanates firstly react with water to producing an intermediate carbamic acid, relatively unstable, that quickly decomposes to yield an amine and CO₂. The resulting amines then react with other isocyanate groups to form urea functions. This mechanism involving water is fundamentally what allows pMDI to thermoset in wood composite conditions. Lastly, during the thermosetting reaction, isocyanates may form biuret or triuret structures from the reaction of an isocyanate function onto an urea. [14], [27]. The isocyanate group can also react with the hydroxyl group of the wood to form urethane bonds link. [27], [28].

Despite those reaction being possible, it is generally accepted during wood panel curing in moisturized conditions that the extension of pMDI with water prevails. The formation of biuret and urethane is usually more favorable at the end of the curing cycle of a wood panel, when moisture is decreasing.

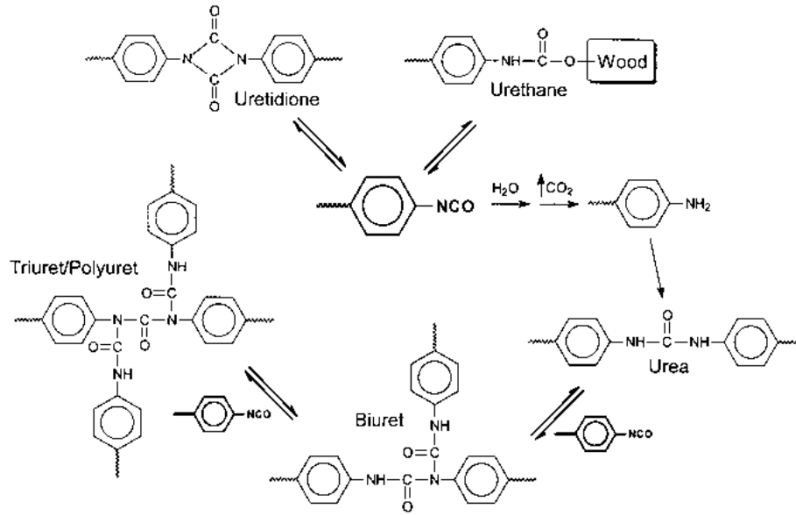


Figure 2.5. Curing mechanism of the pMDI-wood bond line [6]. *Reproduced with permissions from Taylor & Francis Group.*

Although formaldehyde is used during the pMDI synthesis, pMDI resin is known as formaldehyde-free resin as they do not contribute to formaldehyde emissions within wood composite panels after manufacturing. Due to the high bonding performance and good resistance to water exposition, this type of resin is widely employed in producing oriented strand board (OSB) for interior, exterior and structural applications. Low resin loadings provide excellent dimensional stability and load-bearing, making it a very competitive technology for this type of panel. It also has some curing speed advantages compared to more conventional phenol-formaldehyde resins. [1], [8]. pMDI resin can also being used

in medium density fiberboard (MDF) or particle boards (PB) but more confidentially, due to process constraints in some cases. [29]

In some applications, emulsion polymer isocyanates (EPI) which blend pMDI with water-soluble polymer polyvinyl alcohol (PVA) or some other hydroxyl functionalized polymers are utilized. The principle is to reinforce the binding power of a non-thermosetting polymer by adding a thermosetting pMDI, creating a network that contribute to provide high strength. [30] The EPI system is not used for making wood composite panels but rather to glue solid wood pieces together (parquet, window frames, furniture parts, plywood, finger joints and beams), some application requiring load-bearing properties and resistance to water conditions.

2.2. Bio-based Adhesives

Recently, driven by the increasing concern about running out of petroleum resources, an increased focus has been placed on developing environmentally friendly and sustainable adhesives for WBPs. Thus, the bio-based adhesives become to the new promising adhesives for the wood-based panel industry.

2.2.1. Lignin

Lignin is the second most available natural polymer next to cellulose, but highly underutilized [31]. It is an amorphous cross-linked phenolic polymer, which hold promise

as a source material for the synthesis of phenolic resins in wood adhesives. The three type monomers (coniferyl alcohol, synapyl alcohol, and p-coumaryl alcohol) are cross-linked by enzymatic polymerization with ether linkages and condensed linkages. As shown in Figure 2.6, the final structure of lignin are mainly three segments, including guaiacyl (G-type), syringyl (S-type) and p-hydroxyphenol propane (*p*-H-type) [8], [32].

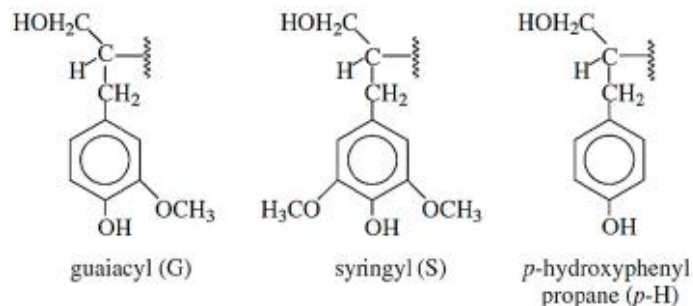


Figure 2.6. The three structural units of lignin [32]. *Reproduced with permission from Elsevier.*

The main type of lignin-based wood adhesives is lignin-based phenol-formaldehyde adhesives, which can be synthesized by inserting formaldehyde into the free *ortho* positions of lignin *via* electrophilic substitution [33]. *p*-H type lignin with two free *ortho* positions and G type lignin with one free *ortho* position can participate in the synthesis [32]. Tejado, et al. stated that Kraft lignin was most suitable for this reaction because it contains most of G-unit with higher molecular weight and larger thermal decomposition energy demand [32]. The bonding performance of the Kraft lignin-based phenol-formaldehyde resin (KLPF) in OSB was investigated by Donmez et al. The result shows by introducing 50wt% Kraft lignin to PF, the elasticity modulus was improved, and the other parameters such as rupture modulus, internal bonding strength, water absorption, swelling thickness remained almost

constant. This indicates that KLPPF could be a promising adhesive for OSB applications [34].

The reactivity of lignin is lower than that of phenols, so chemical modifications like ultrafiltration, demethylation, and methylation are necessary. Olivares, et al. co-polymerize the lignin of *Pinus radiata* black liquor and formaldehyde. Methylation and demethylation are adopted for reactivity improvement. It is concluded that the performance of final products reaches peaks at 18.8% ultra-filtrated high molecular weight lignin, 22.9% phenol and 58.3% formaldehyde [35]. Cetin et al. synthesized a phenolated-organosolv lignin-formaldehyde resin and characterized its performance of bonding PB. When compared to the unmodified lignin-based PF resin, the phenolated lignin PF resin exhibited the better mechanical properties [36].

2.2.2. Starch

Compared with non-renewable petrochemical resources like phenol and formaldehyde, starch emits no volatile organic compound and contains no toxic residual chemicals [37]. In addition to the environmental amity, starch is widely used in the industry as biopolymer for its abundance, low cost, and ease of being obtained from the renewable source [38].

Starch polymer molecules consist in polymers of linear amylose and branched amylopectin both being exclusively homopolymers of α , D-glucose. [39] As shown in

Figure 2.7, starch polymeric units (anhydroglucosidic units) are linked only by (1→4)- α - and (1→6)- α - at branching points in amylopectin. Compared with amylopectin, amylose is a relatively short and linear structure with a molecular weight in the range of $1 \times 10^5 - 1 \times 10^6$. Amylopectin is a larger molecule with molecular weight within the range of $1 \times 10^7 - 1 \times 10^9$, and it contains approximately 95% (1→4)- α - and 5% (1→6)- α - linkages [40].

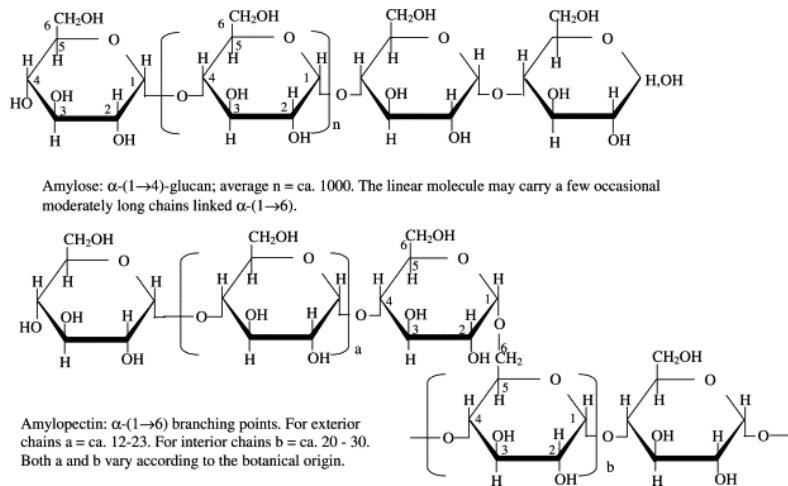


Figure 2.7. Structure of amylose and amylopectin [41]. *Reproduced with permission from Elsevier.*

Starch glue has been extensively applied in adhesive formulations for many years [42], [43]. There are three hydroxyl groups on C2, C3 and C6 position of glucose in starch which can ensure the forming of hydrogen bonding. However, the existence of a large number of hydroxyl groups could result in hydrophilic properties, poor water resistance and slow drying rate to the starch. Esterification is an alternative way to enhance the hydrophobicity of starch through chemical modification. Qiao, et al. proposed a method to react starch with maleic anhydride so that hydroxyl groups could be esterified. After the crosslinking with a

polyisocyanate pre-polymer, the desired product is obtained [44]. Moubarik, et al. used cornstarch and quebracho tannin to replace part of phenol-formaldehyde (PF), and found optimal mechanical properties at a weight ratio of 15:5:80 for cornstarch-quebracho tannin-PF resins [45]. Tan, et al. combined starch and blocked isocyanate with the auxiliary agent, to achieve the highest drying bonding at starch/isocyanate ratio of ratio of 100/20 and highest dry bonding strength at starch/isocyanate ratio of ratio of 100/25 [46]. However, the starch still suffers from the low initial viscosity, poor storage stability and mobility, and insufficient gluing capacity [47].

To overcome these drawbacks, several starch-based wood adhesives (SWA) have been proposed. Grafting copolymerization is a synthesis method to arrange synthetic polymers onto the backbone of starch to improve the bonding properties. Wang, et al. grafted vinyl acetate (VAc) monomers onto starch with ester linkage of the hydroxyl group of the glucose. The enhancement of bonding shows a 59.4% in dry state and 32.1% in the wet state based on shear strength. The water resistance was also reported to have exhibited 61.1% increase. In consideration of economics, a starch/monomer weight ratio of 1:1.2 was recommended [48]. Furthermore, Chen, et al. improved the bonding performance of poly vinyl acetate (PVAc) starch-based wood adhesives by adding butyl acrylate (BA) as another co-monomer for grafting polymerization, which is shown in Figure 2.8. The optimum performance is achieved in the VAc/BA volume ratio of 6:4. The results show 6.68 MPa and 3.32 MPa increasing in dry and wet states of shear strength [49].

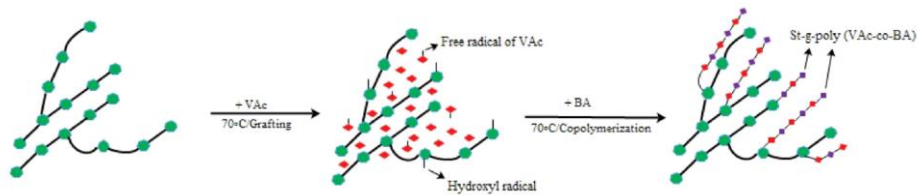


Figure 2.8. Schematic illustration of the grafting reaction of VAc and BA onto starch during the polymerization reaction [49]. *Reproduced with permission from Elsevier.*

The object of investigation for starch adhesive experiments is typically corn starch.

Xu, et al. synthesize environmental-friendly cassava starch-based wood adhesives with butyl acrylate as co-monomer. The cassava starch-based wood adhesives show superior stability than corn starch-based wood adhesives with similar bonding performance [50].

2.2.3. Plant Protein

Plant proteins like soybean protein and canola protein are the other kinds of attractive components for wood adhesives. They are environmentally friendly and easy to obtain from the renewable source. Adhesives containing plant proteins manifest high viscosity and short life cycle [51]. Unsatisfactory bonding performance especially poor water resistance is the main concern that is needed to be solved. The water resistance can be improved by modifying the structure of the protein as well as processability. The following paragraphs will show various types of protein applied in the field of adhesives.

- *Soy protein-based wood adhesives*

Soy protein-based wood adhesive is one of the common plant protein-based adhesives.

As mentioned above, the main drawback of plant protein-based adhesives is poor water

resistance. One method to overcome this is cross-linking. There are several kinds of cross-linkers for soy-based adhesives. Lei, et al. summarized three kinds of cross-linkers which can enhance the water resistance of the soy protein-based adhesives, including epoxy resin, melamine-formaldehyde, and a mixture of epoxy resin and melamine-formaldehyde. The result shows both epoxy and melamine-formaldehyde can react with hydroxyl (–OH) and amine groups (–NH) of soy protein to achieve crosslinking [52]. Liu and Li modified soy protein isolate (SPI) with maleic anhydride (MA) to obtain MA-grafted SPI (MSPI). Compared with the conventional SPI, the MA-grafted SPI has faster formation of ester linkage, superior strength and better water resistance [53]. The subsequent one is called enzymatic modification. Kalapathy, et al. proposed a trypsin-modified soy proteins (TMSP) adhesive and observed the performance on woods. Compared with unmodified SP, double adhesive strength is measured when TMSP reached 2 mg/cm² during cold pressing for soft maple [54]. Chemical denaturation is another method of improve the performance of starch. Rassam incorporated SP into phenol-formaldehyde (PF) resin. This was designed for the composites of recycled old corrugated container (OCC) and wood. 10% Soy/PF resin could bind the composites containing up to 50% OCC flakes for exterior uses [55]. In addition to the methods listed, the use of additives is a relatively simple method for controlled modifications. Carbohydrates is one kind of suitable additives, the water resistance and hydrophobicity can be enhanced when the content of sucrose and glucose increased [56].

- *Canola Protein-Based Wood Adhesives*

After the defat process, Canola as second largest oilseed products are composed of a 30-45wt % protein content and resistant 42-4wt % oil content [57]. In this amount of protein, cruciferin occupies 60% and napin occupies another 20%. Li, et al. incorporated sodium bisulfite (NaHSO_3) into canola protein at different pH values. Impurities were reduced with increasing the concentration of NaHSO_3 : once it reached 3 g/L, the fluid property and ease of operation of the adhesive improved dramatically under the condition of constant wet shear strength [51]. Similar to starch wood adhesives, grafting polymerization with an initiator of free radicals can also be applied in protein-based wood adhesives. As shown in Figure 2.9, Wang, et al. designed reaction method to produce a wood adhesive. The results show increasing thermal stability and water resistance of protein-based adhesive, due to the formation of hydrogen and covalent bonds. It is also concluded that grafting degree at 81.97% can guarantee tighter inter-locking properties with the assistance of chemical reaction at the interlayers between wood surfaces [57].

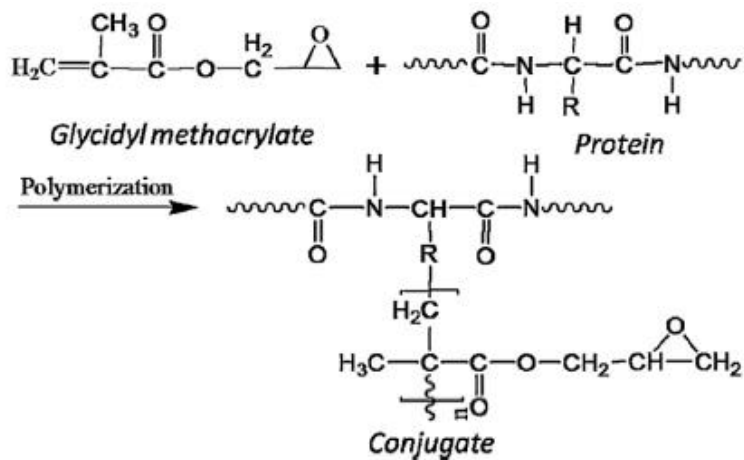


Figure 2.9. The chemical reaction between canola protein and glycidyl methacrylate [57].
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Chapter 3. Behavior of water/pMDI Emulsion Adhesive on Bonding Wood Substrate with Varied Surface Properties

As introduced in Chapter 1, pMDI resin is a non-added formaldehyde (NAF) resin and a versatile chemical capable of reacting with numerous substrates or polymers. The purpose of this chapter is to study the properties of a water/pMDI resin system, to observe how the characteristics of such a system. In the work, an alternative approach to applying pMDI resin was explored, in which water/pMDI emulsions were prepared and then applied to bond wood. This method would provide locally sufficient moisture to cure pMDI in order to study the correlation between bonding strength, bonding failure type and resin penetration depth on a ply model.

The bonding strength of the pMDI resin is influenced by the wood parameters (e.g. species, anatomy, and water content), properties of the adhesive (e.g. viscosity, pH) and the bonding process (e.g. assembly time, temperature and pressure) [58]. Literature shows that penetration depth of the adhesive is also an effective factor that influences the adhesion strength of the bonded wood. The penetration of the adhesive is defined as the movement of liquid adhesive into the porous wood tissue. In general, the penetration of resin can be divided into two levels: micrometer level (gross penetration) and nanometer level (cell wall penetration) [59]. The gross penetration is the result of the resin, which has low viscosity, flows into the porous structure of the wood driving by the capillary action. In contrast, the

cell wall penetration represents that the resin can diffuse into the cell walls, which can only be observed when the resin component has small-molecular-weight [60]. Different methods have been employed to examine the resin penetration [60]–[62]. Fluorescence microscopy (FM), light microscopy (LM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used for visualizing the gross penetration of resin. For the cell wall penetration, UV-microscopy, electron energy loss microscopy, chemical-state X-ray microscopy, confocal laser scanning microscopy (CLSM), and scanning thermal microscopy can be used [60]. As the pMDI has low viscosity, low molecular weight, and low surface tension, it can readily wet the wood surface and penetrate deeply into the wood structure [6], [63]. However, to the best of our knowledge, there is no clear correlation between the penetration depth and the final bonding strength.

In this work, we first investigated the optimum content of water in the formulated water/pMDI adhesive for the best adhesion bonding. After that, wood substrates were modified by (3-aminopropyl) triethoxysilane (APTES) to introduce amine group onto the wood surface and improve the interaction between the pMDI and wood substrate. The penetration depth of adhesive in the wood substrate was also investigated to explain the decline of bonding strength on high concentration APTES treated wood substrates.

3.1. Experimental section

3.1.1. Materials

Polymethylene diphenyl diisocyanate (pMDI) utilized in this work was supplied by BASF (LUPRANATE® M20 Isocyanate). pMDI is a dark amber liquid mixture which contains mainly pMDI (40% to 70%), partly diphenylmethane-4,4'-diisocyanate (4,4'-MDI, 30% to 60%) and little methylenediphenyl diisocyanate (less than 5%). The average molar mass of this pMDI mixture is 360 g/mol and the average isocyanate functionality is around 3. All other chemicals, including (3-aminopropyl) triethoxysilane (APTES), the silane coupling agent; oil red O, the red dye for pMDI; and ethanol, the solvent, were purchased from Sigma-Aldrich and used as received. Pinewood substrates which were utilized as the substrate for the bonding strength test were supplied by First Voice (Tongue depressor, No-sterile, Model: First Voice TS-4312-500).

3.1.2. Water/pMDI Adhesive Emulsion

To prepare the water/pMDI emulsion, various weight ratios of water (from 5 to 50wt%) was added into pMDI, a planetary centrifugal THINKY Mixer (ARE-310, in STD mode), was used for mixing process (3 min at 2000 rpm) and defoaming process (2 min at 2200 rpm). The mixture was further homogenized by using a Vortex Mixer (Fisherbrand™ Analog) for 10 min at 3200 rpm to obtain a uniform emulsion.

3.1.3. Wood Surface Modification

In order to further improve the bonding strength of the adhesive, the wood substrates were modified by pre-treatment with APTES to introduce amine groups onto the wood surface. Following the protocol in the literature [64], two APTES solutions (1 and 3wt%) in ethanol/water (80/20 by weight/weight) were prepared by vigorously stirring for 2 h at room temperature. Wood specimens were then immersed in each APTES solution for 30 minutes and dried at 120 °C for 1 h. After drying, the samples were washed with deionized water and ethanol to remove the un-bonded APTES. The samples were dried at 120 °C to remove all the solvent.

3.1.4. Characterization

3.1.4.1. Viscosity

The viscosity of the water/pMDI emulsion was measured by a viscometer (Brookfield CAP 2000+ with the cone spindle (Model: No. 1)), at room temperature (23 °C) and constant shear rate (1333 1/s). For each data point, three independent measurements were carried out to calculate the average viscosity. The viscosity of each formulated emulsion was measured every hour (5 hours in total) to monitor the viscosity variation over time.

3.1.4.2. Contact Angle

The performance of the wood substrates pre-treatment was evaluated by contact angle measurement. NE-1010 Higher Pressure Syringe Pump was used to pump out a 5 μ L water

droplet or pMDI droplet onto the neat or pre-treated wood substrates. An in-house custom-made Contact angle goniometer was utilized to record the contact angle and the pictures of contact angle were analyzed by the scientific image analysis software ImageJ.

3.1.4.3. Pull-off Test

To test the bonding strength of the water/pMDI adhesive, the pull-off test was conducted based on ASTM D4541–17 standard [65] to determine the stress required to detach the stub from the wood substrate (shown as Figure **3.1a**). To simulate the application of pMDI adhesive in the wood industry, wood on wood pull-off test was performed by attaching a circular shape wood disk (0.5-inch diameter) onto a same size pin stub with epoxy adhesive. Afterward, the certain amount of (0.03 g/cm²) water/pMDI emulsion was applied uniformly on the neat or APTES-treated wood substrates, and then the coated wood specimen was put gently on the top of the wood bonded pin stub and cured in a preheated oven at 160 °C for 5 h under 50 kPa pressure. Six samples were prepared for each formulated adhesive and all of the wood substrates used in the test were pre-dried in the oven at 120 °C until mass constant. The cured samples were cooled down and stored in the sealed zip-lock bag for 3 days. After 3 days, the prepared samples were examined by a universal materials tester (UMT, UNMT-2MT) with constant loading rater (0.1 mm/s) at room temperature (23 °C) and relative humidity 30%.

3.1.4.4. Single Lap-shear Test

The single lap-shear test is another test method utilized to determine the bonding

strength of the water/pMDI adhesive. It was conducted based on ASTM D1002-10 standard [66] to measure the required shear stress to detach the bonded wood samples. To fabricate the samples for the single lap-shear test (Figure 3.1b), the pre-dried neat or APTES-treated wood substrates was cut into a rectangle shape (0.5 in \times 3 in). A small square wood (0.5 in \times 0.5 in) was glued on one side of the cut wood substrate by epoxy resin to make a holder for the shear test sample. On the other side of the cut wood substrate, the same amount (0.03 g/cm²) formulated water/pMDI emulsion was applied to the small surface (0.5 in \times 0.5 in). Then, the wood substrate was put onto another one with the adhesive-coated surface overlapped. Afterward, the sample was cured in a preheated oven at 160 °C for 5 h under 50 kPa pressure. Five samples were prepared for each specifically formulated wood adhesive. After storing the samples at room temperature for 3 days, the single lap-shear test was performed by a tensile testing machine (INSTRO 4465) with a constant speed of 3mm/min at room temperature (23 °C) and relative humidity 30%.

3.1.4.5. Penetration Depth of pMDI

To evaluate the penetration depth of pMDI in the neat or APTES-treated wood substrate, differential staining method was applied by coloring the pMDI specifically with oil red O. Shown as Figure 3.1c, certain amount of oil red O (1mg/g of pMDI) was firstly dissolved in pMDI, and then 30wt% of water was added into the colored pMDI. After the same procedure of preparing the adhesive emulsion, the formulated adhesive (0.03 g/cm²) was applied on two wood substrates homogeneously, and then the coated wood specimens

were put together and cured at 160 °C for 5 h at 50 kPa pressure. After cooling to the room temperature, the cross-section of the cured sample was cut and observed by a digital microscope (Dino-Lite Premier AM3113T 2.0). The penetration result was determined by analyzing the sample cross-section image with ImageJ. The penetrated line of pMDI in the cross-section is described as the deepest straight-line which is parallel to the bonding interface and goes through at least five detected pMDI objects (red spots inside the wood structure), and the penetration depth is defined as the distance between the interface of two bonded wood substrates and the penetrated line of pMDI [62]. Eight samples were prepared for each specific wood (neat wood, 1wt% APTES-treated wood, 3wt% APTES-treated wood).

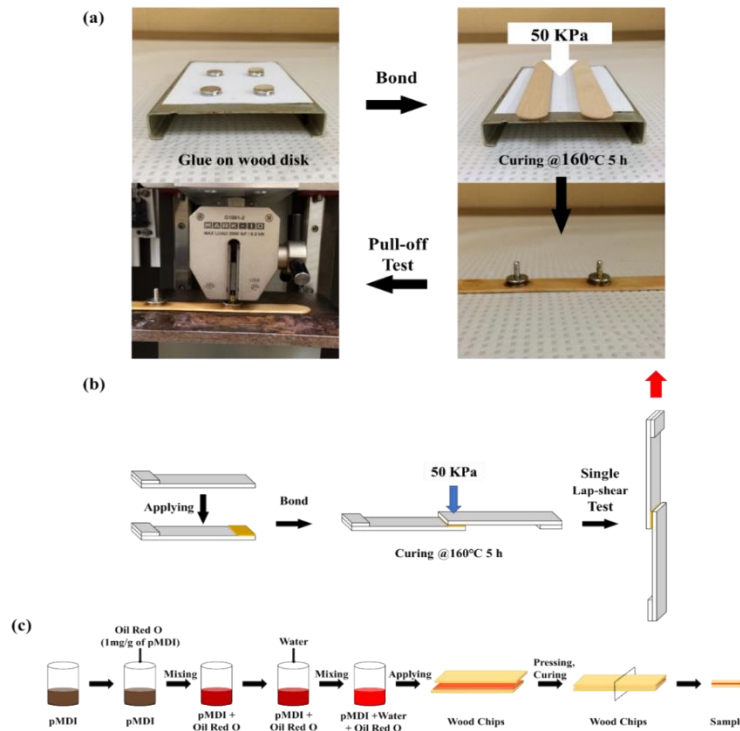


Figure 3.1. Sample preparation and testing procedure for (a) pull-off adhesion test (b) single lap-shear test (c) penetration of pMDI characterization

3.2. Results and Discussion

3.2.1. Suitable Dye for pMDI

To determine the microstructure of the adhesive emulsion and characterize the penetration behavior of the adhesive on the wood substrate, staining method was applied in this work. As pMDI is the effective component of the water/pMDI adhesive, a suitable dye that can color the pMDI specifically should be firstly selected to demonstrate its morphology and behavior. From the literature, Safranin O (the chemical structure is shown as Figure **3.2a**) is a commonly used fluorochrome dye to stain the adhesives and demonstrate them under the fluorescence microscope [62], [67], [68]. However, this dye is not appropriate for water/pMDI adhesives because of its low solubility in pMDI (Figure **3.2b**). The Safranin O powder is more soluble in water, which indicates it would more likely trace water rather than pMDI during the penetration process. In order to characterize the pMDI penetration behavior specifically, a pMDI-soluble but water-insoluble dye is needed in this work. Oil Red O (the chemical structure is shown in Figure **3.2c**), a lysochrome diazo dye which is initially used in histology to stain the fat or lipids in tissues [69], was chosen for the water/pMDI adhesive. Figure **3.2d** shows Oil Red O has a good solubility in pMDI and almost insolubilize in water. This indicates Oil Red O can demonstrate the penetration behavior of pMDI specifically.

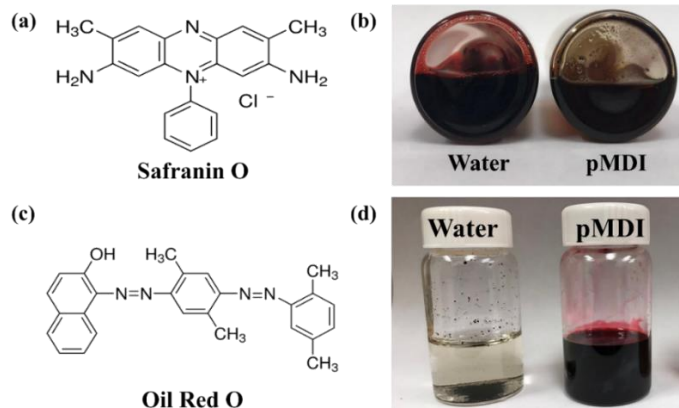


Figure 3.2. (a) Chemical structure of Safranin O. (b) Solubility of Safranin O in water and pMDI. (c) Chemical structure of Oil Red O. (d) Solubility of Oil Red O in water and pMDI. The concentration of dye in water or pMDI: 1mg/g solvent.

The thermal stability is another critical criterion to evaluation the dye. As the water/pMDI adhesive needs to be cured at 160 °C for 5 hours, the dye must be stable at this high temperature. The thermogravimetric analysis (TGA) result shows the good thermal stability of Oil Red O at 160 °C as it starts to decompose at around 230 °C (Figure 3.3a). Furthermore, the water solubility of Oil Red O at 160 °C was also checked (Figure 3.3b), the Oil Red O is still water-insoluble and can trace pMDI specifically at this high temperature. To investigate the adhesive penetration behavior, water/pMDI adhesive was firstly mixed with the dye, applied to the wood substrate and finally cured in the oven. To identify the penetrated component is colored pMDI or undissolved Oil Red O powder, the control group of applying pure Oil Red O₃ powder onto the wood substrate has been done. The cross-section image of the wood specimen shows there is no red spot in the wood structure which means by following the same procedure, the pure Oil Red O powder cannot penetrate into wood substrates. Therefore, combining the solubility, thermal stability and

penetration result, the Oil Red O can be determined as the suitable dye to demonstrate pMDI specifically in the emulsion morphological structure characterization and the pMDI penetration behavior investigation.

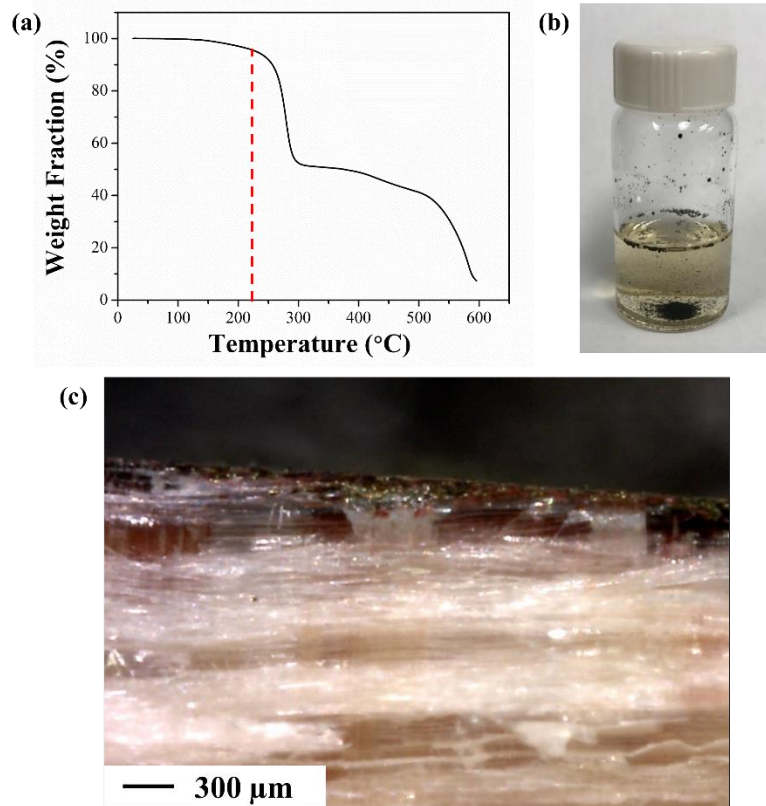


Figure 3.3. (a) Thermogravimetric analysis curve of Oil Red O (heating rate 10°C/min) (b) Solubility of Oil Red O in water at 160°C. (c) Photographs of the cross-section the wood specimen with Oil Red O.

3.2.2. Optimal Water Content in Water/pMDI adhesive

In this work, the water/pMDI emulsions were prepared and then applied on to dry wood substrates. This approach is different from the conventional method of directly applying pMDI resin on wood materials that contain a finite amount of moisture [6], [27], [70]. The advantage of this emulsion approach is that it allows a localized addition of water

within the pMDI to provide sufficient reagent for curing and also provides an opportunity to add other biopolymer fillers into pMDI for next step investigation. For now, this work focused on the water/pMDI system only and the first objective was to determine the optimal water content in the emulsion in terms of emulsion stability and the pull-off adhesion tests and lap-shear adhesion tests.

Figure 3.4 shows the stability of the water/pMDI emulsions. Macroscopically, water/pMDI emulsions are uniform and stable when the water concentration is less than 35wt%. Phase separation of water and pMDI is observed when the water concentration is over 40wt% (Figure 3.4a). With the aid of Oil Red O, it is easy to distinguish water phase and pMDI phase under the microscope. From the microscope image (Figure 3.4b), it can be seen that the microscopic water droplets disperse in the pMDI suggesting this is a water in the pMDI emulsion; which means water and pMDI act as the dispersion phase and the continuous phase, respectively. For water concentration less than 35wt%, the distribution of the size of water drops is narrow; but the size of water drops gradually increases with the increasing concentration of water. For the water concentration greater than 40wt%, both the size and the size distribution of water droplets greatly increase. Water/pMDI emulsions appear to transform from the uniform state to phase separation at the concentration of water is over 40wt%. Therefore, only the uniform emulsions (water content <35wt%) were applied to bonding performance test.

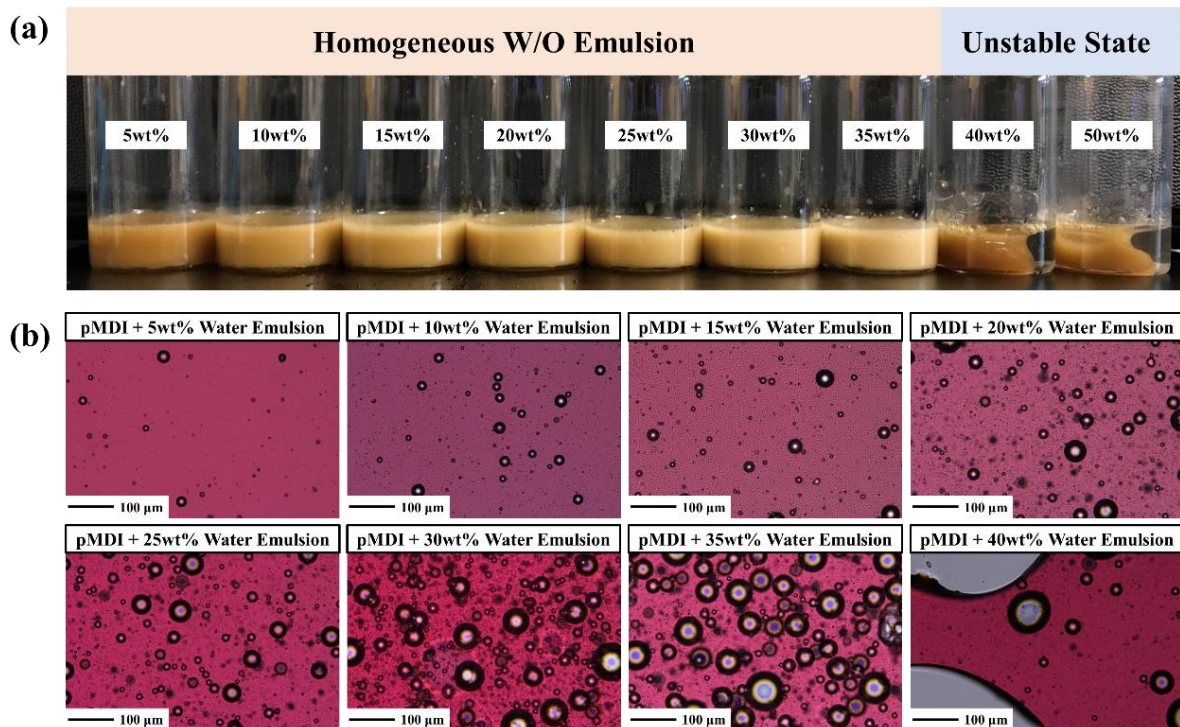


Figure 3.4. (a) Photographs of water/pMDI emulsions of different constitutions. (b) Optical microscope images of water/pMDI emulsions of different constitutions.

The viscosity of the water/pMDI emulsions was measured over a certain period of storage time (**Figure 3.5a**). As expected, the viscosity of the emulsions increase with time and water concentration, suggesting that some curing reaction leading to an increase of molecular weight takes place once water and pMDI are mixed even at room temperature. pMDI curing is composed of two consecutive steps (**Figure 3.5b**) in which the reaction between pMDI and water molecules produces carbon dioxide and an amine by decomposition of a carbamic acid, followed very quickly by the reaction of the resulting amine with another isocyanate function to form a urea linkage [6], [27], [28]. The generation of carbon dioxide over time was verified by sealing some emulsions in a syringe

to observe the volume expansion over time (Figure 3.5c).

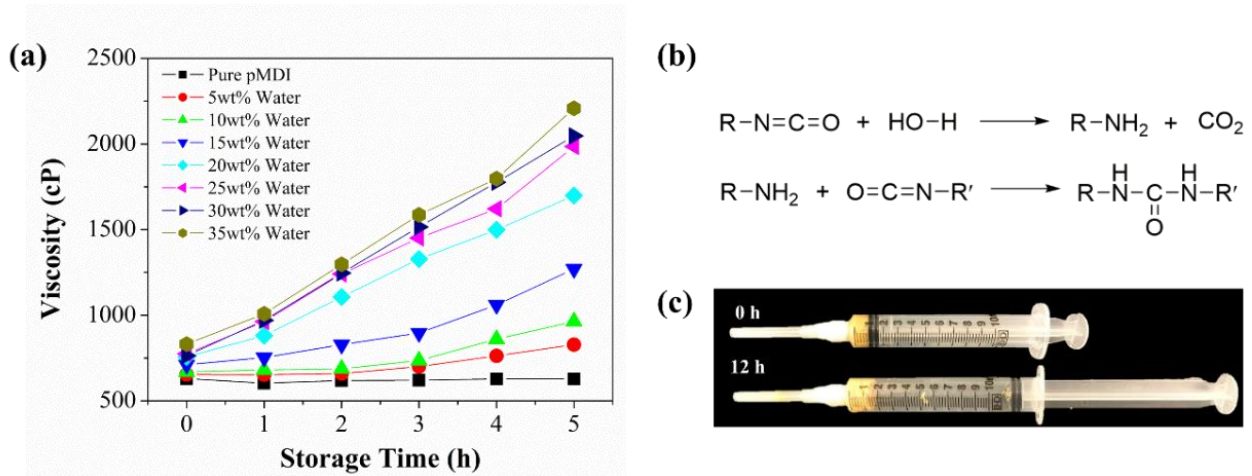


Figure 3.5. (a) Dependence of the viscosity of water/pMDI emulsions on the water concentration and storage time. (b) The mechanism for the reaction between pMDI and water to generate the polyurethane. (c) Photographs of the water/pMDI emulsions in the sealed syringe at initial state and storage for 12 h at room temperature.

To ensure wetting and spreading of the water/pMDI emulsion on wood substrates so as to form good adhesive bonds, the emulsions were applied on the surface of the wood substrates within one hour after mixing to avoid high viscosity. For the bonding process, the emulsions were first coated on the surface wood substrates, and then the coated wood specimen was put gently on the top of an array of wood bonded pin stubs (for pull-off test), or another piece of wood substrate (for lap-shear test). Finally, the bonded samples were cured in a preheated oven at 160 °C for 5 h under 50 kPa pressure. The 160 °C curing temperature is to accelerate the reaction between pMDI, water as well as wood structure and the 5 hours curing time is to make sure the reaction is completed.

To investigate the effect of water content on the bonding performance of the water/pMDI adhesive, the pull-off test, and single lap-shear test were constructed on the

neat wood substrates. Figure **3.6a** shows the pull-off stress almost linearly increases with the increasing concentration of the water until reaching the maximum value, 1.25 MPa, with the 30wt% water concentration. when the water concentration is over 30wt%, the pull-off stress slightly decreases. As shown in the lap-shear test result (Figure **3.6b**), the changing trend of lap-shear stress as the concentration of water is similar to that of the pull-off test. The lap-shear stress can be as high as 5 MPa. The dependence of the pull-off and lap-shear stress on the concentration of the water both illustrates that the bonding strength of wood adhesives enhances with the higher concentration of the water before the concentration of the water reaches 30wt%.

The effect of the constitution of emulsions on the bonding strength of wood adhesives can be more directly observed at the failure surface of the samples after the pull-off and lap-shear tests (Figure **3.6c** and **3.6d**). At relatively lower water concentration (<15wt%), some wood adhesives are observed at the failure surface indicating the failure happens in the internal of the adhesives, which is named as the cohesive failure of the adhesive [71]. At relatively higher water concentration (>20wt%), more and more wood fibers can be seen at the failure surface indicating the failure occurs at the wood substrates, which is named as the cohesive failure of the wood [72]. As both the pull-off and lap-shear test measure the stress needed to detach the bonded sample, the failure usually happens at the weakest link of the bond. Thus, the cohesive failure of wood is preferable than the cohesive failure of adhesive, indicating the adhesive bond is stronger than the substrate [14]. Combining the

bonding performance and the previous emulsion stability, it could be concluded as 30wt% water content is determined as the optimum water content to the water/pMDI adhesive, as it can form a homogenous adhesive emulsion and provide the highest bonding strength on the neat wood.

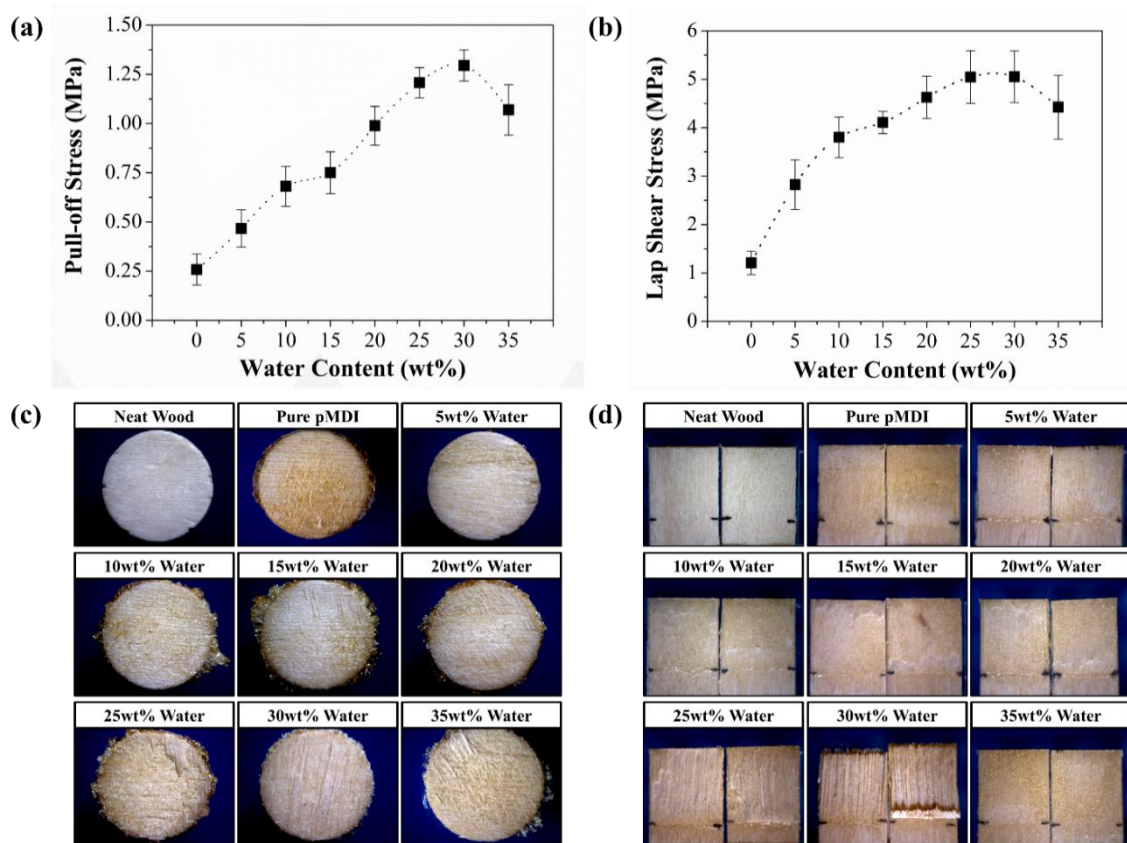


Figure 3.6. Dependence of the (a) pull-off stress and (b) lap-shear stress on the concentration of the water in the emulsions. Photographs of the failure surface of the samples with different concentrations of water after (c) the pull-off and (d) lap-shear test.

3.2.3. Silanized Wood Substrates

In addition to the adhesive composition, the bonding strength can also be modulated through the modification of the wood substrates since both the adhesives and wood

substrates are important for the bonding strength. The silane coupling agent APTES was utilized to modify the wood substrates; we hypothesized that APTES might be capable of enhancing the interaction between the adhesives and wood substrates since it contains amine groups that have a good molecular affinity to pMDI. The mechanism of APTES treatment is shown in Figure 3.7, the ethoxy groups in the APTES can hydrolyze rapidly to ethanol and tri-silanol. Then, the silanol groups may react with the surface hydroxyl groups of the wood substrates leading to surface silanization [73].

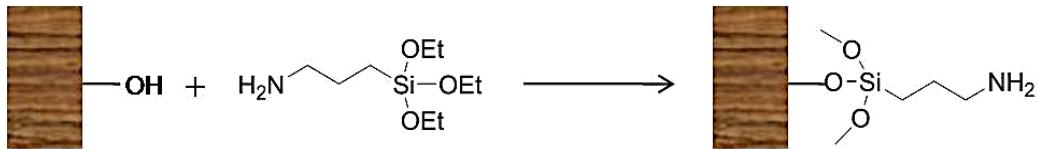


Figure 3.7. The mechanism for the reaction between wood substrates and APTES.

The noticeable changes in contact angle verified the successful modification of the wood substrates by APTES [74]. As shown in Figure 3.8a, the water contact angles are larger on the APTES-treated wood substrates but pMDI contact angles are smaller on the APTES-treated wood, suggesting that the wood substrates become more hydrophobic but more pMDI-philic. Afterward, the adhesive with 30wt% water content was chosen to investigate the influence of the modification of the wood substrates on the bonding strength. Figure 3.8b and 3.8c show that the bonding strength first increases and then decreases with the increasing concentration of APTES. This observation seems to contradict the fact that stronger interaction between the adhesives and wood substrates leads to the larger bonding

strength. We suspect that this contradiction might be related to the penetration of the adhesives.

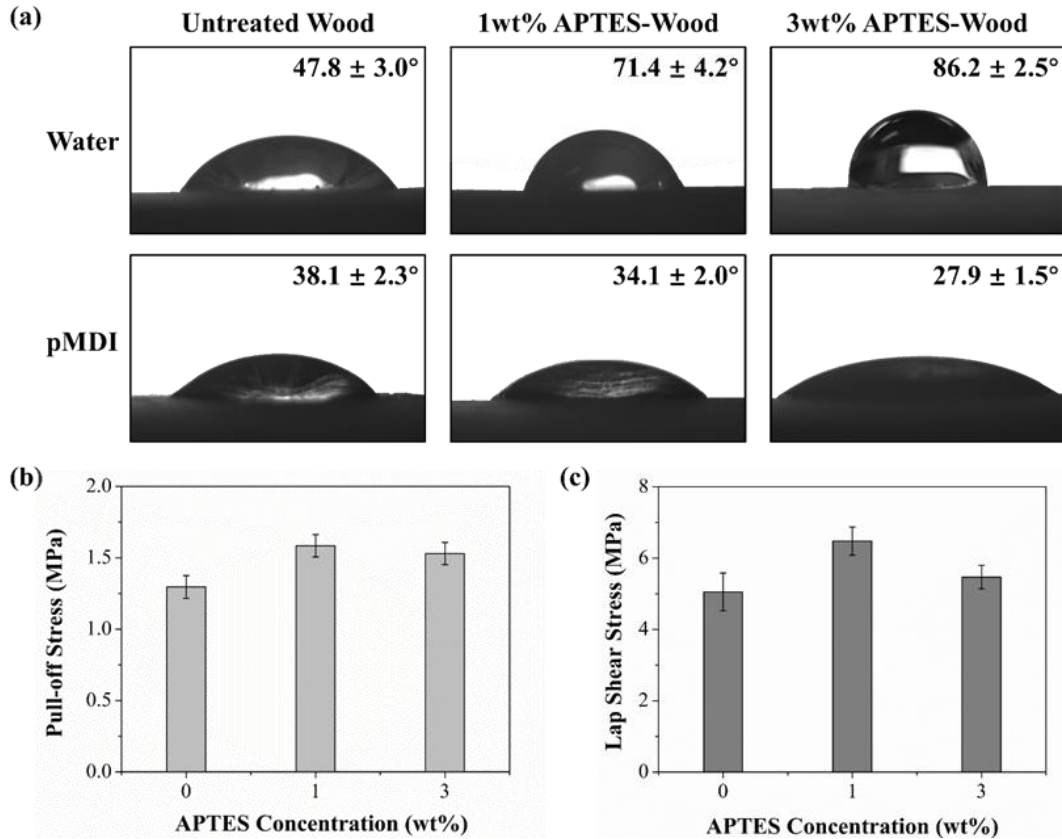


Figure 3.8. (a) Water or pMDI contact angle on the surface of pure wood substrates, 1wt% or 3wt% APTES modified wood substrates. Dependence of the (b) pull-off stress and (c) lap-shear stress on the concentration of APTES for wood treatment.

3.2.4. Penetration of pMDI

To investigate the penetration of the adhesives, we doped the adhesives by pMDI soluble and water insoluble dye as pMDI is the effective component of the adhesives. Thus, we can easily characterize the penetration of the adhesives by observing the distribution of dye-doped adhesives in the cross-section of the wood substrates using the microscope. To

quantify the penetration behavior of the adhesives, we determine the penetration depth defined as the distance of the liquid adhesive moved into the porous wood structure [62]. In the cross-section, the penetration depth is measured as the distance between the bonding line and the adhesive penetrated line. For reference, the only porous structure was seen in pure wood substrates (Figure 3.9a). In the cross-section of the adhesive bonded wood substrates, some red dots corresponding to the dye-doped adhesives are clearly observed around the bonding line (Figure 3.9b-d).

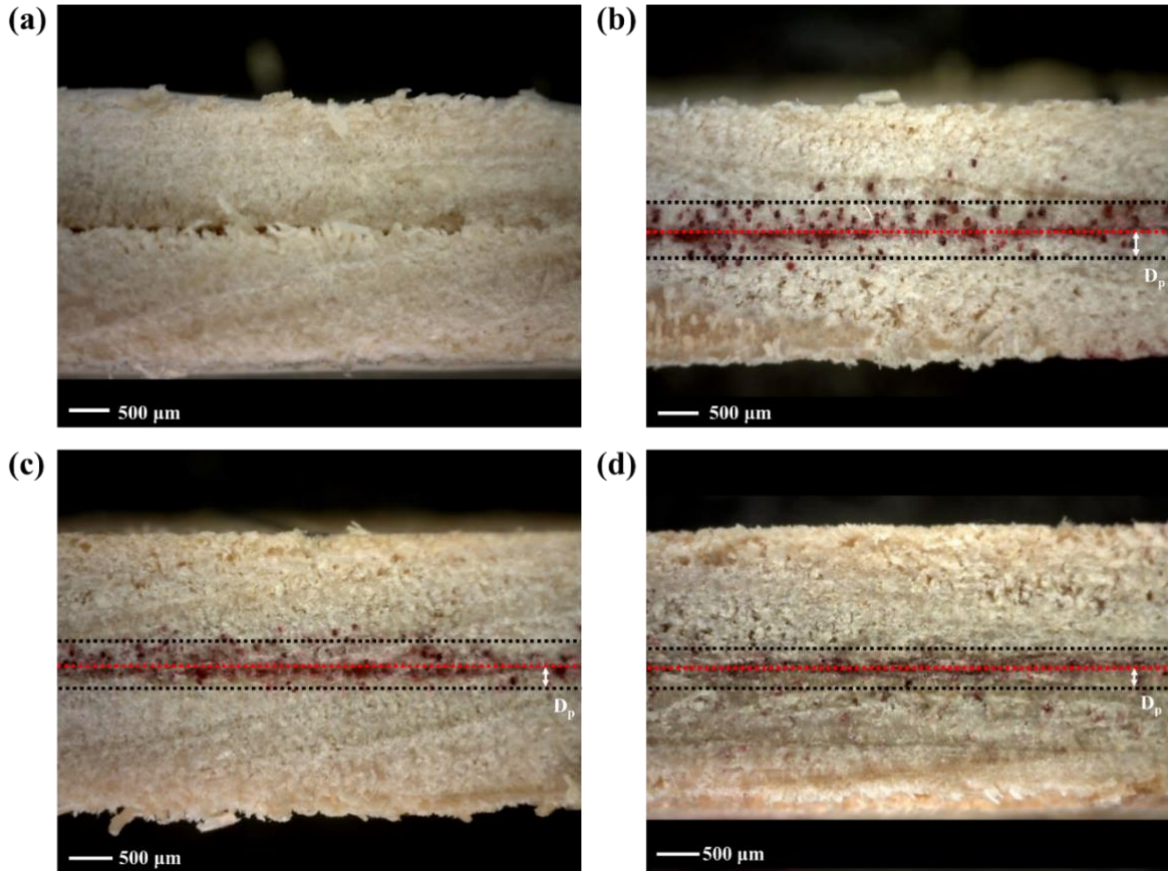


Figure 3.9. (a) Photographs of the cross-section of neat wood substrates. Photographs of the cross-section of (b) neat wood substrates and wood substrates modified by (c) 1wt% and (d) 3wt% APTES bonded by dye-doped adhesives.

Table 3.1. The penetration of pMDI on different types of wood substrates.

Types of Wood	Depth of pMDI Penetration (μm)
Neat Wood	341 ± 31
1wt% APTES-Wood	281 ± 23
3wt% APTES-Wood	210 ± 29

Although the wettability of pMDI on the wood substrates is enhanced by the modification of APTES (Figure 3.8a), the penetration depth reduces as the APTES concentration increases (Table 3.1). Combining with the penetration result, we were able to explain the effect of the modification of the wood substrates on the bonding strength. Without the modification of the wood substrates, it shows the lowest bonding strength due to the relatively weaker interaction between the adhesives and wood substrates. In addition, over penetration (penetration depth of $341 \pm 31 \mu\text{m}$) results in a small portion of the adhesives remaining at the interface of two bonded wood substrates that cannot provide enough mechanical property of the adhesives. When the wood substrates are modified by 1wt% APTES, it shows the highest bonding strength due to enhanced interaction between the adhesives and wood substrates and moderate penetration (penetration depth of $281 \pm 23 \mu\text{m}$). The strongest interaction between the adhesives and wood substrates is achieved when the wood substrates are modified by 3wt% APTES. However, the bonding strength decreases because of insufficient penetration (penetration depth of $210 \pm 29 \mu\text{m}$) inducing the limited contact of the adhesives and wood substrates leads the lack of

chemical/mechanical bonding [75].

3.3. Conclusions

In summary, we investigated the behavior of water/pMDI emulsions and its bonding performance as a wood adhesive. A pMDI soluble but water-insoluble dye was doped into water/pMDI emulsions in order to determine the microstructure of the emulsions and penetration behavior of the adhesives on the wood substrate. The results show that the emulsions consist of water droplets dispersed in continuous pMDI and are stable enough to provide a workable adhesive within a timeframe of 1 h when water contents are less than 35wt%; phase separation is observed at higher water contents probably due to phase inversion or poor stability in the absence of surfactant. Both the pull-off and lap-shear tests suggested that 30wt% water led to the highest bonding strength on the neat wood substrate. By the modification of the wood with silane coupling agent APTES, we were able to modulate the interaction between the adhesives and wood, pMDI wettability and penetration in the substrate. The results show that strong interactions between the adhesives and wood substrate and a certain level of penetration of the adhesives are required for good bonding performance where excessive penetration might be detrimental to the adhesive bonding strength.

Chapter 4. Concluding Remarks and Recommendations

4.1. Conclusions

The objective of this project is to evaluate the performance of an experimental grade biopolymer as a co-binder of pMDI resin for bonding wood. To achieve this aim, a water/pMDI adhesive was first studied as a baseline. The stability and phase separation of water/pMDI emulsion were examined by image analysis and viscosity measurements. The effects of the emulsion composition on the bonding strength of the adhesive were determined by both the pull-off and lap-shear tests, showing an optimal water content around 30wt%. The bonding strength was further improved by modification of the surface of the wood substrate using the silane coupling agent APTES. The silanization process changes surface hydrophilicity and adhesive penetration depth so as to improve the adhesive bonding strength. The results show that a moderate penetration enhances bonding strength, providing insights into the non-proportional relationship between adhesive penetration and bonding strength.

For the biopolymer/pMDI adhesive, the effect of the biopolymer to the pMDI resin is studied by comparing the biopolymer/pMDI adhesives with the water/pMDI adhesives. The biopolymer can work as a stabilizer, emulsifier and thickener to yield an adhesion system where portion of pMDI can be replaced without affecting strength. The emulsion characteristics and viscosity of the resultant adhesive emulsion can be changed by dilution

which makes it a versatile adhesive system for composite panels but as well in applications beyond it where lower and higher viscosity than native pMDI are desired. The results showed that a biopolymer/pMDI adhesive system demonstrates the same bonding strength than pMDI alone. Overall, the biopolymer can be used as a co-binder to pMDI resin, to reduce the dosage of pMDI and increase bio-based renewable content within a non-added formaldehyde system for wood applications.

4.2. Future work

In this project, the wood substrate utilized in the adhesion test is the small pieces of pine wood block, which is easy to obtain and operate. In the next step, to simulate the fabrication of the WBPs, the wood substrates should be explored to another wood materials such as wood chips, fibers, plies, veneer.

After characterizing the biopolymer/pMDI adhesive in lab scale, the performance of this adhesive should be further investigated at industrial scale. To produce the WBPs, the industry process like hot pressing, should be applied to the biopolymer/pMDI adhesive. Future research is needed to design the process conditions, including temperature, loading pressure, time for press, adhesive loading quantities and so on. After that, the performance of the product panels such as strength, water resistance, formaldehyde emission and durability should be evaluated and compared with the other commercial products.

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